

- **COORDINATION COMPOUND**
- **METALLURGY**
- **D-BLOCK**
- **SALT ANALYSIS**

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THEORY AND EXERCISE BOOKLET

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JEE SYLLABUS

• COORDINATION COMPOUND

JEE - ADVANCED

Coordination compounds: nomenclature of mononuclear coordination compounds, cis-trans and ionisation isomerisms, hybridization and geometries of mononuclear coordination compounds (linear, tetrahedral, square planar and octahedral).

• METALLURGY

JEE - ADVANCED

Orbital overlap and covalent bond; Hybridisation involving s, p and d orbitals only; Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral).

• d-BLOCK

JEE - ADVANCED

Transition elements (3d series): Definition, general characteristics, oxidation states and their stabilities, colour (excluding the details of electronic transitions) and calculation of spin-only magnetic moment; Preparation and properties of the following compounds: Oxides and chlorides of tin and lead; Oxides, chlorides and sulphates of Fe^{2+} , Cu^{2+} and Zn^{2+} ; Potassium permanganate, potassium dichromate, silver oxide, silver nitrate, silver thiosulphate.

• SALT ANALYSIS

JEE - ADVANCED

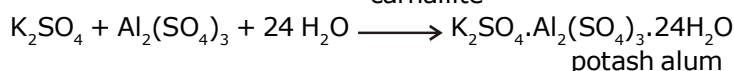
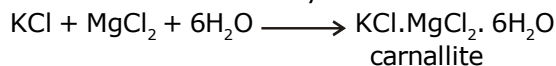
Groups I to V (only Ag^+ , Hg^{2+} , Cu^{2+} , Pb^{2+} , Bi^{3+} , Fe^{3+} , Cr^{3+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Mn^{2+} and Mg^{2+}); Nitrate, halides (excluding fluoride), sulphate, sulphide and sulphite.

COORDINATION COMPOUND KEY CONCEPTS

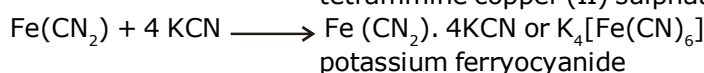
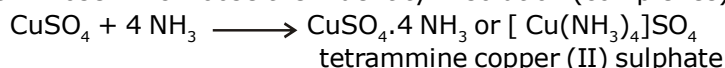
Molecular / Addition Compound :

Molecular / Addition compounds are formed when stoichiometric amounts of two or more simple compounds join together. Molecular / Addition compounds are of two types.

Double salts : Those which retain their identity in solutions are called double salts. For example.



Complex compounds : Those which lose their identity in solution (complexes). For example.



When crystals of carnallite are dissolved in water, the solution shows properties of K^+ , Mg^{2+} and Cl^- ions. In a similar way, a solution of potash alum shows the properties of K^+ , Al^{3+} and SO_4^{2-} ions. These are both examples of double salts which exist only in the crystalline state. When the other two examples of coordination compounds are dissolved they do not form simple ions, Cu^{2+} / Fe^{2+} and CN^- , but instead their complex ions are formed.

Representation of Complex Ion :



when

M = Central Metal atom /ion (usually of d-block)

L = Ligand

x = No. of ligands

n^\pm = charge on coordination

Outside region apart from coordination sphere is called ionisation sphere.

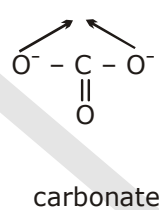
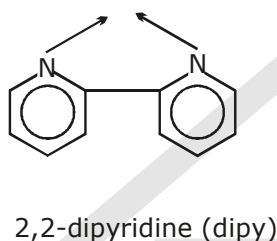
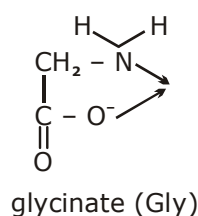
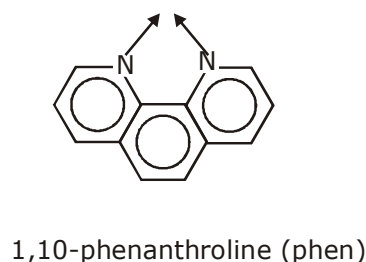
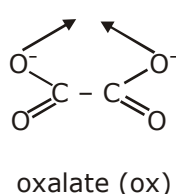
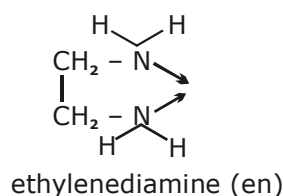
- 1. Central metal atom/ion :** Central ion acts as an acceptor (Lewis acid) and has to accommodate electron pairs donated by the donor atom of the ligand, it must have empty orbitals. This explains why the transition metals having empty d-orbitals form co-ordination compounds readily. Thus, in complexes $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$, Ni^{2+} and Fe^{3+} respectively are the central metal ions.
- 2. Ligands :** Species which are directly linked with the central metal atom/ ion in a complex ion are called ligands. The ligands are attached to the central metal atom /ion through co-ordinate or dative bond free ligands have at least one lone pair.



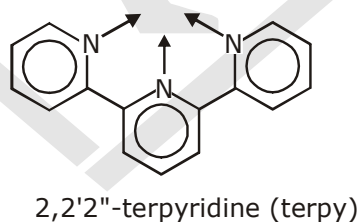
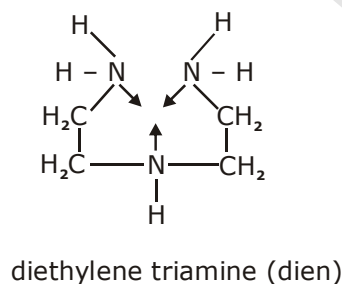
The ligands are thus Lewis bases and the central metal ions / atoms are Lewis acids.

Ligands can be of following types depending on the number of donor atoms present in them.

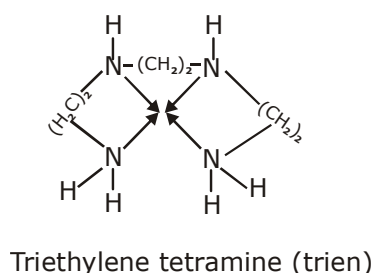
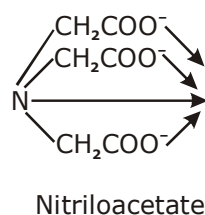
- (i) **Mono / Unidentate Ligands** They have one donor atom, i.e., they can donate only one electron pair to the central metal atom/ion eg., F^- , Cl^- , Br^- , H_2O , NH_3 , CN^- , NO_2^- , OH^- , CO etc.
- (ii) **Bidentate Ligands** Ligands which have two donor atoms and have the ability to link with the central metal atom/ion at two positions are called bidentate ligands e.g.



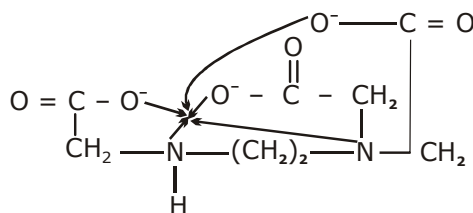
- (iii) **Tridentate Ligands** Ligands having three donor atoms are called tridentate ligands. Examples are



- (iv) **Tetradentate Ligands** These ligands possess four donor atoms. Examples are

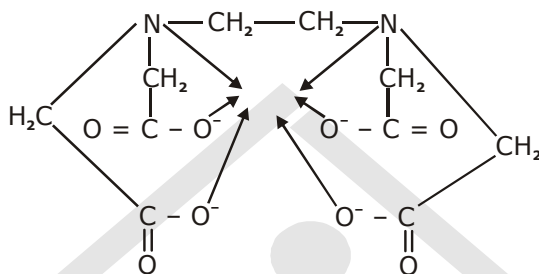


(v) **Pentadentate Ligands** They have five donor atoms. For example, ethylenediamine triacetate ion.



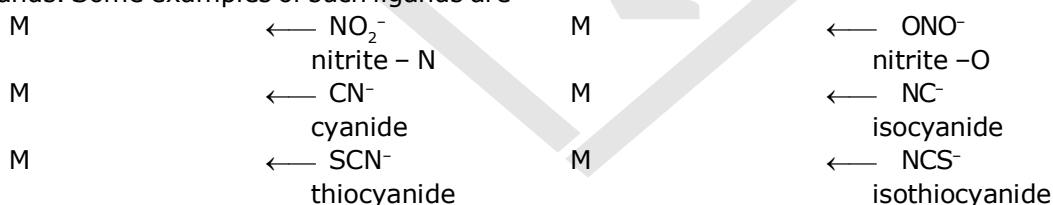
ethylenediamine triacetate ion

(vi) **Hexadentate Ligands** They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



ethylenediamine tetraacetate (EDTA)

(vii) **Ambidentate ligands** : There are certain ligands which have two or more donor atoms but in forming complexes, only one donor atom is attached to the metal / ion. Such ligands are called ambidentate ligands. Some examples of such ligands are



(viii) Ligands having more than two donor atoms are called polydentate or multidentate ligands. Multidentate ligands are known as a chelating ligands, it results in the formation of a stable cyclic ring thus, the complexes formed are also called chelates. Chelating ligands are usually organic compounds.

3. **Co-ordination sphere** The central metal atom and the ligands directly attached to it are collectively termed as the co-ordination sphere. Co-ordination sphere is written inside square brackets, for examples, [Co(NH₃)₆]³⁺. Remember that the central metal atom and the ligands inside the square brackets, behave as a single entity.

4. **Co-ordination number (CN)** The co-ordination number (CN) of a metal atom /ion in a complex is the total number of e⁻ pairs accepted by central metal atom /ion from ligands through coordinate bond. Some common co-ordination numbers of metal ions are summarised in the following Table (1) and examples of complexes of various co-ordination number are given in Table (2).

Table (1) Co-ordination number of metal ion

Metal ion	Co-ordination number
Ag ⁺	2,4
Cu ⁺	2,4
Cu ²⁺	4,6
Au ⁺	2,4
Ca ²⁺	4,6
Fe ²⁺	4,6
Fe ³⁺	6
Co ²⁺	4,6
Co ³⁺	6
Ni ²⁺	4,6
Zn ²⁺	4
Al ³⁺	4,6
Sc ³⁺	6
Cr ³⁺	6
Pd ²⁺ , Pt ²⁺	4
Pd ⁴⁺ , Pt ⁴⁺	6

Table (2) Examples of complexes of various co-ordination numbers

Complex	Co-ordination number
[Ag(NH ₃) ₂] ⁺	2
[HgI ₃] ⁻	3
PtCl ₄ ²⁻ , Ni(CO) ₄	4
Fe(CO) ₅ , [Ni(CN) ₅] ³⁻	5
[Co(NH ₃) ₆] ³⁺ , W(CO) ₆	6
[Mo(CN) ₇] ³⁻	7
[Mo(CN) ₈] ⁴⁻	8

5. Oxidation number/oxidation state (O.S.) of central metal ion It is a number (numerical value) which represents the electric charge on the central metal atom of a complex ion. For example the oxidation number of Fe, CO and Ni in [Fe(CN)₆]⁴⁻, [Co(NH₃)₆]³⁺ and Ni(CO)₄ are +2, +3 and zero, respectively. Let us take a few examples to illustrate this.

(i) Potassium Ferrocyanide, K₄[Fe(CN)₆] Since the complex has four monovalent cations outside the coordination sphere, the complex ion must carry four negative charges, i.e., it is [Fe(CN)₆]⁴⁻. The number of CN⁻ ion (univalent ion), that is 6 represents the co-ordination number of Fe cation. The oxidation state of iron can be determined easily as below, knowing that cyanide ions are unidentate and the complex on the whole carries -4 charge.

$$\begin{aligned}
 &[\text{Fe}(\text{CN})_6]^{-4} \\
 &x + (-6) = -4 \\
 \therefore &x = +2
 \end{aligned}$$

Thus, here iron is present as Fe²⁺ or Fe(II).

- (ii) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ Note that here the oxalate ligand is a negative ion, that is it is bidentate. Therefore three oxalate ligands carry a total charge of -6 and co-ordination number of Cr is 6. Now since the complex carries -3 charge, therefore the oxidation state of Cr is $+3$.
- (iii) $\text{Ni}(\text{CO})_4$ Here the co-ordination number of Ni is 4 since carbonyl group is unidentate. Further since the complex as well as the ligands has no charge, nickel atom must also be neutral, that is it is in zero oxidation state.
6. **Effective atomic number -EAN (Sidgwick Theory and EAN Rule) :** Total no. of electrons present on central metal atom/ion. after accepting electron pairs from donor atom of ligands through coordinate bond is called E.A.N. of central metal atom/ion.

$$\text{E.A.N} = Z - \text{O.S.} + 2 \times \text{C.N.}$$

Sidgwick also suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of nearest noble gas. This total number of electrons is called effective atomic number (EAN) of the metal/ion. This will become clear by taking the example of hexamminecobalt (III) ion $[\text{Co}(\text{NH}_3)_6]^{3+}$

Atomic number of cobalt = 27

In the present complex, cobalt is present in the oxidation state of $+3$.

$$\begin{aligned}\therefore \text{E.A.N. of Co}^{3+} &= Z - \text{O.S.} + 2 \times \text{C.N.} \\ &= 27 - 3 + 2 \times 6 = 36\end{aligned}$$

In the above example since the number 36 corresponds to the atomic number of krypton, according to Sidgwick, the complex will be stable. Though EAN rule (which states that those complexes are stable whose EAN is the same as the atomic number of the next noble gas) is applicable in many metal carbonyl complexes, however there are several examples in which EAN rule is not obeyed.

IUPAC NOMENCLATURE OF COMPLEXES :

The rules for the systematic naming of co-ordination compounds are as follows.

- (i) The positive part is named first followed by the negative part, whether it is simple or complex.
- (ii) In naming of a complex ion, the ligands are named first in alphabetical order, followed by naming of central metal atom/ion.
- (iii) When there are several monodentate ligands of the same kind, then we normally use the prefixes di, tri, tetra, penta and hexa to show the number of ligands of that type. If ligand's name already contains any of these prefixes, then to avoid confusion in such cases, bis, tris and tetrakis are used instead of di, tri and tetra and name of the ligand is placed in parenthesis. For example, bis(ethylene diamine) for two en-ligands.
- (iv) Negative ligands have suffix -o, positive ligands have suffix -ium, whereas neutral ligands have no specific suffix.

The names of negative ligands ending with -ide are changed to 'o'. For example,

F^-	fluoro /fluorido	H^-	hydrido	HS^-	mercapto
Cl^-	chloro /chlorido	OH^-	hydroxo/hydroxido	S^{2-}	sulphido
Br^-	bromo / bromido	O^{2-}	oxo / oxido	CN^-	cyano / Cyanido
I^-	iodo / iodido	O_2^{2-}	peroxo / Peroxido		

Ligands ending with -ate/-ite are changed to -ato/-ito. For example, SO_4^{2-} (sulphato), SO_3^{2-} (sulphito) etc.

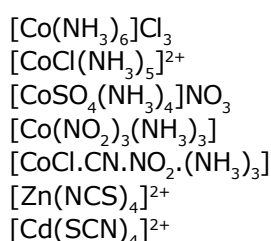
Positive groups end with -ium. For example, $\text{NH}_2 - \text{NH}_3^+$ (hydrazinium) NO^+ (nitrosonium)

- (v) Neutral ligands have No special ending and usually common ligands are provided to neutral ligands except NH_3 (ammine) H_2O (aqua) CO (carbonyl), NO (Nitrosyl).
- (vi) The oxidation state of the central metal ion is shown by Roman numeral in brackets immediately following its name.
- (vii) Complex positive ions and neutral molecules have no special ending but complex negative ions end with ate. suffix.

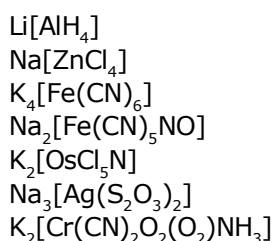
Table (3) Complex ions

Example	Negative complex	Positive / neutral complex
Ni	nickelate	nickel
Pb	plumbate	lead
Sn	stannate	tin
Fe	ferrate	iron

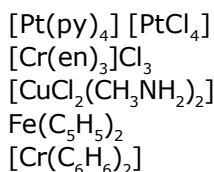
- (viii) If the complex compound contains two or more metal atoms, then it is termed as polynuclear Complex compound. The bridging ligand which link the two metal atoms together are indicated by the prefix μ^- . If there are two or more bridging groups of the same kind, this is indicated by di- μ^- , tri - μ^- and so on. If a bridging group bridges more than two metal atoms, it is shown as μ_3 , μ_4 , μ_5 or μ_6 to indicate how many atoms it is bonded.
- (ix) Ambidentate ligands may be attached through different atoms. Thus, $\text{M}-\text{NO}_2$ is called nitro and $\text{M}-\text{ONO}$ is called nitrito. Similarly $\text{M}-\text{SCN}$ (thiocyanato) or $\text{M}-\text{NCS}$ (Isothiocyanato). These may be named systematically, thiocyanato-S and thiocyanate -N respectively to indicate which atom is bonded to the metal. This convention may be extended to other cases where the mode of linkage is ambiguous.
- (x) If any lattice component such as water or solvent of crystallisation are present, these follow their name, and are preceded by the number of these groups in Arabic numerals. These rules are illustrated by the following examples.

(a) Complex cations**IUPAC name**

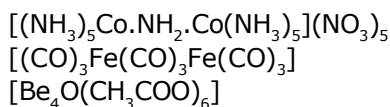
Hexaamminecobalt(III) chloride
 Pentaamminechloridocobalt(III) ion
 Tetraamminesulphatocobalt(III) nitrate
 Triamminetrinitrito-N-cobalt(III)
 Triammine-chloro-cyano-nitro-N-cobalt(III)
 Tetrathiocyanato-N-zinc(II) ion.
 Tetrathiocyanato-S-cadmium(II) ion.

(b) Complex anions

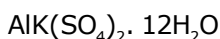
Lithium tetrahydridoaluminate(III)
 Sodium tetrachloridozincate(II)
 Potassium hexacyanidoferrate(II)
 Sodium pentacyanidonitrosyliumferrate(II)
 Potassium pentachloridonitridoosmate(VI)
 Sodium bis(thiosulphato)argentate(I)
 Potassium amminedicyanidodioxidoperoxidochromate(VI)

(c) Organic groups

tetrapyridineplatinum(II) tetrachloridoplatinate(II)
 d or ℓ Tris(ethylenediamine) chromium(III)chloride
 Dichloridodimethylaminecopper(II)
 Bis(η^5 -cyclopentadienyl)iron(II)
 Bis(η^6 -benzene)chromium(0)

(d) Bridging groups

μ -amidobis[pentaamminecobalt(III) nitrate]
 Tri- μ -carbonyl-bis [tricarbonyliron(0)]
 Hexa- μ - acetato(O,O')- μ_4 -oxidotetraberyllium(II)
 (basic beryllium acetate)

(e) Hydrates

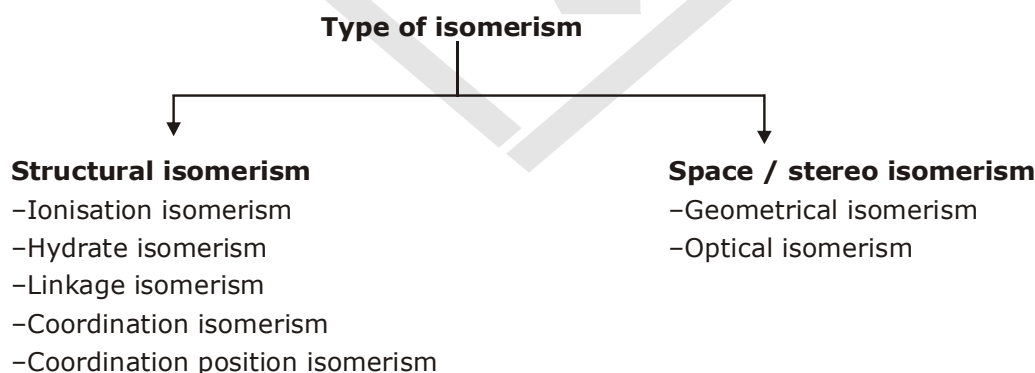
Aluminium potassium sulphate 12-water

Writing the formula of a coordination compound :

When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is named first, then the coordinated groups are listed in the order : negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group).

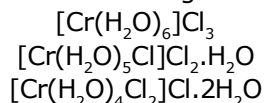
[M negativel ligands, Neutral ligands, positive ligands] $_{\pm}$ **ISOMERISM IN COMPLEXES :**

Complex compounds that have the same molecular formula but have different structural /spacial arrangements of ligands are called isomers. These are of two types, namely structural and stereo isomers.

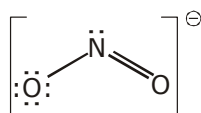
**Structural Isomerism**

- (i) Ionisation Isomerism** This type of isomerism is due to the exchange of groups between the complex ion and ions outside it. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ is red -violet. An aqueous solution of it gives a white precipitate of BaSO_4 with BaCl_2 solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ is red. A solution of this complex does not give a positive sulphate test with BaCl_2 . It does give a creamcoloured precipitate of AgBr with AgNO_3 , thus confirming the presence of free Br^- ions. Other examples of ionisation isomerism are $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$ and $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$ and $[\text{Co}(\text{en})_2\text{NO}_2.\text{Cl}]\text{SCN}$, $[\text{Co}(\text{en})_2\text{NO}_2.\text{SCN}]\text{Cl}$ and $[\text{Co}(\text{en})_2\text{Cl}.\text{SCN}]\text{NO}_2$.

- (ii) **Hydrate isomerism** These isomers arise by the exchange of groups in the complex ion with water. Three isomers of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ are known. From conductivity measurements and quantitative precipitation of the ionised Cl^- , they have been given the following

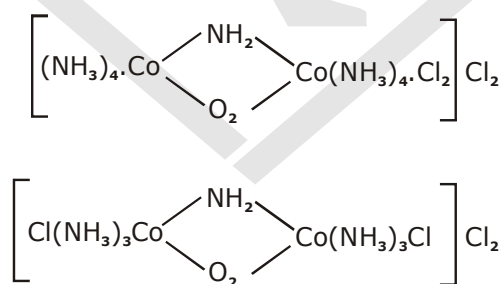


- (iii) **Linkage Isomerism** This type of isomerism arises when the ligand attached to the central metal ion of a complex in different ways. Such ligands are called ambident ligands. Nitrite ion has electron pairs available for co-ordination both on N and O atoms.



Examples

- (a) $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$
 pentaamminenitrito-o-cobalt(III) chloride pentaamminenitrito-N-cobalt-(III)-chloride
 (red) (yellow)
- (b) $[\text{Mn}(\text{CO})_5\text{SCN}]^+$ and $[\text{Mn}(\text{CO})_5(\text{NCS})]^+$
 pentacarbonylthiocyanato pentacarbonylthiocyanato
 -S-manganese (II) ion -N-manganese (II) ion
- (iv) **Co-ordination Isomerism** When both the cation and anion are complex ions, then isomerism may be caused by the interchange of ligands between the anion and cation. For example $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{PtCl}(\text{NH}_3)_3][\text{PtCl}_3(\text{NH}_3)]$. These isomers are called co-ordination isomers.
- (v) **Co-ordination Position Isomerism** In polynuclear complexes, an interchange of ligands between the metal nuclei gives rise to co-ordination position isomerism, for example.



Co-ordination position isomers

Polymerisation Isomerism : This is not true type of isomerism because it occurs among compounds having the same empirical formula, but different molecular formula. Thus, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{NH}_3)\text{Cl}_3]$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2[\text{PtCl}_4]$ all have the same empirical formula.

Stereo Isomerism

These are the isomers in which ligands have different spatial arrangements around central metal atom / ion in 3-D space.

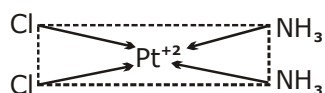
Geometrical is Isomerism Geometrical isomers are the isomers in which the atoms are joined to one another in the same way but differ in space because some ligands occupy different relative positions in space.

Geometrical Isomerism in complex compound having C.N. = 4

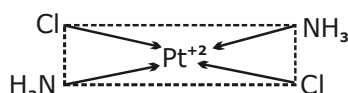
Tetrahedron complexes (sp^3 hybridisation) never exhibit geometry isomerism, however, it is very common in square planer complexes (dsp^2 hybridisation).

For Example

(a) $[Pt(NH_3)_2Cl_2]$ can exist as two geometrical isomers.

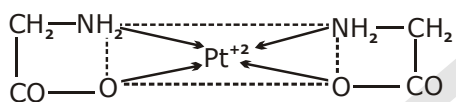


cis form (orange yellow)



trans form (pale yellow)

(b) $[Pt(Gly)_2]$ also exist in two geometrical isomers.



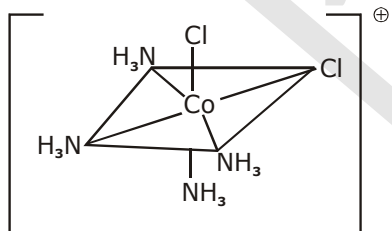
cis form



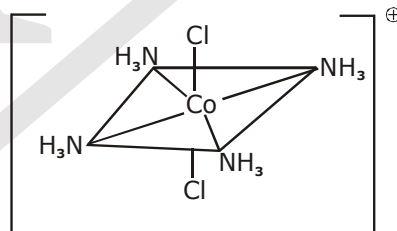
trans- form

Geometrical Isomerism in Complex compound having co-ordination number 6

(a) $[Co(NH_3)_4Cl_2]^+$ can exist as

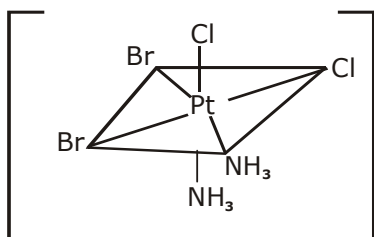


cis form (violet)

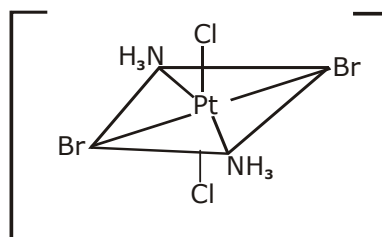


trans form (green)

(b) $[Pt(NH_3)_2Cl_2Br_2]$ can exist as



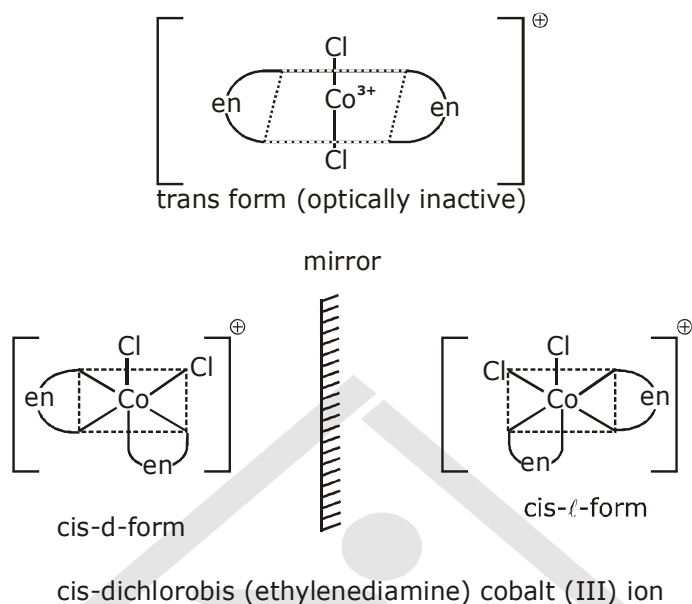
cis



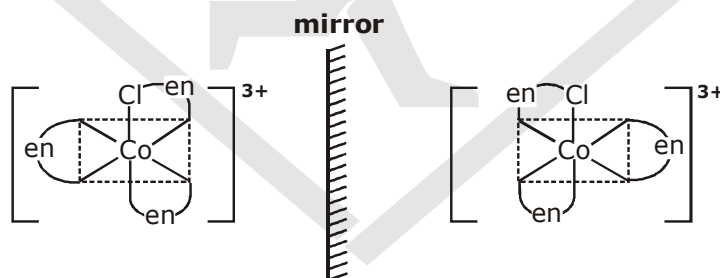
trans

There are many more trans arrangements.

- (ii) **Optical Isomerism** If a molecule is asymmetric then it cannot be superimposed on its mirror image. These forms are called optical isomers. They are called either dextro or laevo compounds depending on the direction in which they rotate the plane polarised light in polarimeter.
- (iii) Optical isomerism is common in octahedral complexes involving bidentate ligand.
- (iv) $[\text{Co}(\text{en})_2\text{Cl}_2]^{\oplus}$ exist as cis-and trans-isomers. But only cis-isomer can have d and ℓ optical isomers.



- (v) Optical isomers of $[\text{Co}(\text{en})_3]^{3+}$ are



BONDING IN COMPLEXES

Werner's Co-ordination Theory :

Alfred Werner put forward his concept of secondary valency for advancing a correct explanation for the characteristics of the coordination compounds. The fundamental postulates of Werner's theory are as follows.

- (i) Metal possess two types of valencies, namely, primary (principal or ionisable) valency and secondary (auxillary or non-ionisable) valency.
- In modern terminology, the primary valency corresponds to oxidation number and secondary valency to coordination number. According to werner primary valencies are shown by dotted lines and secondary valencies by thick lines.

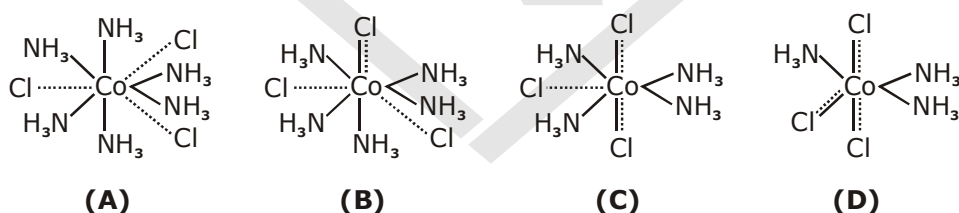
- (ii) Every metal cation in complex compound has a fixed number of secondary valencies for example Pt^{4+} cation has its six secondary valency.
- (iii) Primary valency is satisfied by negative ions, whereas secondary valency is satisfied either by negative ions or by neutral molecules.
- (iv) Primary valency has non-directional character, whereas secondary valency has directional character, therefore a complex ion has its definite geometry eg. $[\text{Co}(\text{NH}_3)_6]^{3+}$ – octahedron.
- (v) It is the directional nature of secondary valency due to which co-ordination compound exhibits the phenomenon of isomerism.

Werner's Representation of Complexes

Consider the case of $\text{CoCl}_3 \cdot x\text{NH}_3$ where primary valency = +3 and secondary valency = 6.
Various structures are summarised in Table -4.

	Werner complexes	Modern formula	Ionisation	Secondary valency satisfied by	Primary valency satisfied by
(A)	$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$	six (NH_3)	three (Cl^-)
(B)	$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$	five (NH_3) and one (Cl^-)	three (Cl^-) including one (Cl^-) with dual nature
(C)	$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$	four (NH_3) and two (Cl^-)	three (Cl^-) including two (Cl^-) with dual nature
(D)	$\text{CoCl}_3 \cdot 3\text{NH}_3$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	three (NH_3) and three (Cl^-)	three (Cl^-) all with dual nature

- * From Table 4, It is clear that conduction of the complexes will be in the order $\text{D} < \text{C} < \text{B} < \text{A}$.
- * They are represented as



Valence Bond Theory :

It was developed by Pauling. The salient features of the theory are summarised below :

- (i) Under the influence of a strong field ligands, the electrons of central metal ion can be forced to pair up against the Hund's rule of maximum multiplicity.
- (ii) Under the influence of weak field ligands, electronic configuration of central metal atom / ion remains same.
- (iii) If the complex contains unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons, then it is diamagnetic in nature and magnetic moment is calculated by spin only formula.

$$\text{Magnetic moment } (\mu) = \sqrt{n(n+2)} \text{ BM}$$

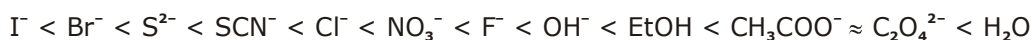
where n is the number of unpaired electrons in the metal ion.

Table 5 Relation between unpaired electrons and magnetic moment

Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

Thus, the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

- (iv) When ligands are arranged in increasing order of their splitting power then an experimentally determined series is obtained named as spectrochemical series.



_____ Weak field ligands _____



_____ Strong field ligands _____

- (v) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands.
The number of empty orbitals is equal to the co-ordination number of the metal ion for a particular complex.
- (vi) The atomic orbital (s, p or d) of the metal ion hybridise to form hybrid orbitals with definite directional properties. These hybrid orbitals now accept e^- pairs from ligands to form coordination bonds.
- (vii) The d-orbitals involved in the hybridisation may be either inner (n – 1) d orbitals or outer n d-orbitals. The complexes formed in these two ways are referred to as inner orbital complexes and outer orbital complexes, respectively.

Limitations of valence bond theory

- (i) Correct magnetic moment of complex compounds can not be theoretically measured by Valence bond theory.
- (ii) The theory does not offer any explanation about the spectra of complex (i.e., why most of the complexes are coloured).
- (iii) Theory does not offer any explanation for the existence of inner -orbital and outer -orbital complexes.
- (iv) In the formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, one electron is shifted from 3d to 4p orbital. The theory is silent about the energy availability for shifting such an electron.
Such an electron can be easily lost then why does not $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex show reducing properties?

Crystal Field Theory (CFT) :

Crystal field theory is now much more widely accepted than the valence bond theory. It is assumed that the attraction between the central metal and ligands in a complex is purely electrostatic. The transition metal which forms the central atom cation in the complex is regarded as a positive ion of charge equal to the oxidation state. It is surrounded by negative ligands or neutral molecules which have a lone pair of electrons. If the ligand is a neutral molecule such as NH_3 , the negative end of the dipole in the molecule is directed toward the metal cation. The electrons on the central metal are under repulsive forces from those on the ligands. Thus, the electrons occupy the d orbital remain away from the direction of approach of ligands.

In the crystal field theory, the following assumptions are made.

- (i) Ligands are treated as point charges.
- (ii) There is no interaction between metal orbitals and ligands orbitals.
- (iii) All the d orbitals on the metal have the same energy (that, is degenerate) in the free atom. However, when a complex, is formed, the ligands destroy the degeneracy of these orbitals, that is , the orbitals now have different energies. In an isolated gaseous metal ion, all five d orbitals have the same energy and are termed degenerate. If a spherically symmetrical field of ligands surrounds the metal ion, the d orbitals remain degenerate. However, the energy of the orbitals is raised because of repulsion between the field of ligands and electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both these cases, the field produced by the ligands is not spherically symmetrical. Thus, the d orbitals are not all affected equally by the ligand field.

In the an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners.

The direction x, y and z point to three adjacent corners of the octahedron as shown fig.

The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes x,y and z. The lobes of the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) point in between the axes. It follows that the approach of six ligands along the x,y,z, -x, -y, and -z directions will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals (which point along the axes) than it increases the energy of the d_{xy} , d_{xz} and d_{yz} orbitals (which points between the axes). Thus, under the influence of an octahedral ligand field the d orbitals split into two groups of different energies. Rather than referring to the energy level of a isolated metal atom. The difference in energy between the two d levels is given by the symbols Δ_0 or $10 Dq$.

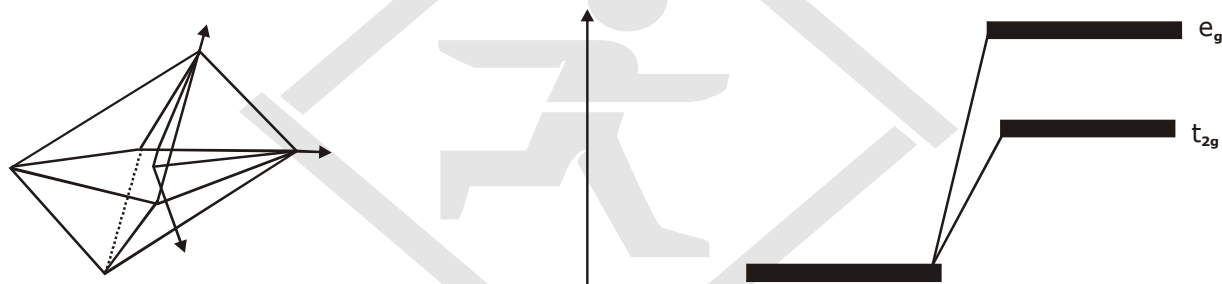


Fig. The directions in an octahedral complex

**Free metal ion
(five degenerate d orbitals)
Fig Crystal field splitting of energy
levels in an octahedral field**

**metal ion in
octahedral field**

It follows that the e_g orbitals are $+0.6 \Delta_0$ above the average level, and the t_{2g} orbitals $-0.4 \Delta_0$ below the average level.

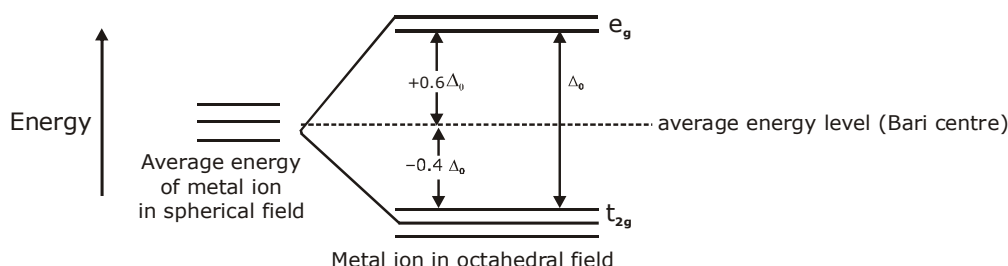


Fig. Diagram of the energy levels of d -orbitals in a octahedralfield

Tetrahedral Complexes A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Fig. The direction x, y and z point to the centres of the faces of the cube. The e_g orbitals point along x, y and z (that is, to centres of the faces.)



Fig. Relation of tetrahedron to a cube

The approach of the ligands raised the energy of both sets of orbitals. The energy of the t_{2g} orbital raised most because they are closest to the ligands. This crystal field splitting is opposite to that in octahedral complexes. The t_{2g} orbitals are $0.4 \Delta_t$ above the average energy of the two groups (the barycentre) and the e_g orbitals are $0.6 \Delta_t$ below the average level.

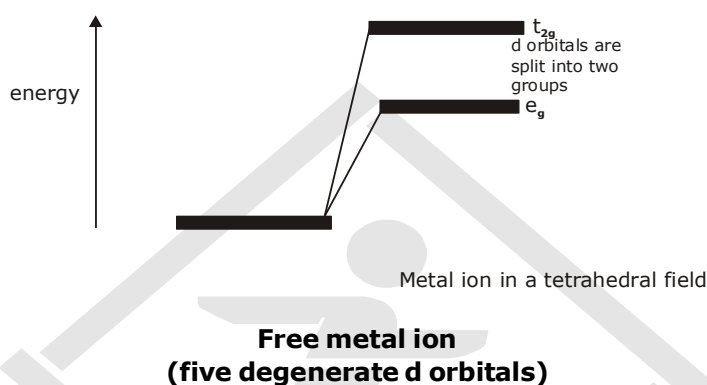
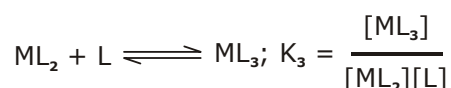
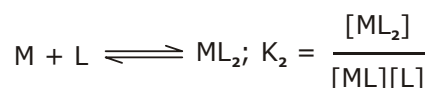
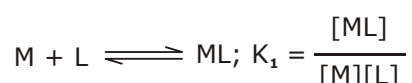


Fig Crystal field splitting of energy levels in a tetrahedral field

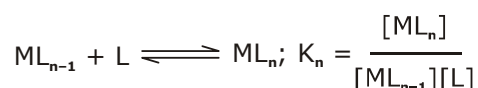
Stability of complexes

A co-ordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex, ML_n (M = central metal cation, L = monodentate ligand and n =co-ordination number of metal ion) supposed to take place by the following n consecutive steps.

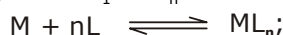


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$K_1, K_2, K_3, \dots, K_n$ are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n . The overall stability constant K is given as



$$K = K_1 K_2 K_3 \dots K_n = \frac{[ML_n]}{[M][L]^n}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively, $1/K$ values called instability constant explain the dissociation of the complex into metal ion and ligands in the solution. The value of the stability constant for some of the complexes are given in Table.

Table : Stability constants of complexes

Complex	Stability constant
$[Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$[Ag(NH_3)_2]^+$	1.6×10^7
$[Co(NH_3)_6]^{2+}$	1.12×10^6
$[Co(NH_3)_6]^+$	5.0×10^{33}
$[AgCl_2]^-$	1.11×10^5
$[AgBr_2]^-$	1.28×10^7
$[Ag(CN)_2]^-$	1.0×10^{22}
$[Cu(CN)_4]^{2-}$	2.0×10^{27}
$[Fe(CN)_6]^{3-}$	7.69×10^{43}

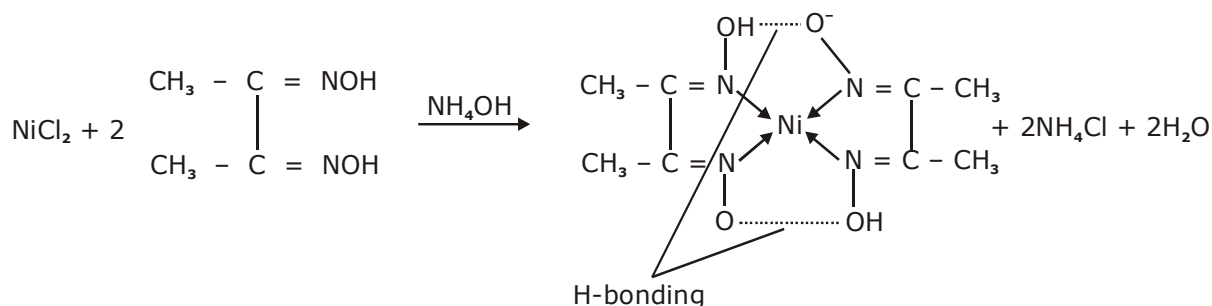
Factors affecting stability of complex compounds :

- The values of stability constant differ widely depending on the nature of the metal ion and the ligand. In general, higher the charge density on the central ion, the greater the stability of its complexes.
 - the more basic a ligand, the greater is the ease with which it can donate its lone pairs of electrons and therefore, greater is the stability of the complexes formed by it.
- eg.** The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that NH_3 and CN^- are strong Lewis bases.
- The higher the oxidation state of the metal, the more stable is the complex. The charge density of Co^{3+} ion is more than Co^{2+} ion and thus, $[Co(NH_3)_6]^{3+}$ is more stable than $[Co(NH_3)_6]^{2+}$. Similarly, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$.
 - Chelating ligands form more stable complexes as compared to monodentate ligands.

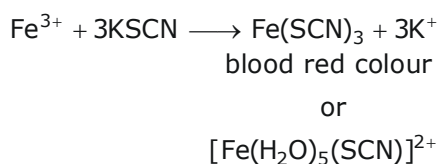
Application of complexes

The complexes are of immense importance on account of their applications in various fields. During complex formation there are drastic changes in the properties of metal atom/ion. These changes in properties are made use of in the application of metal complexes.

- The detection and estimation of Ni^{2+} is based on the formation of a scarlet red complex with dimethyl glyoxime.



- (a) Fe^{3+} is detected by formation of a blood red coloured complex with KSCN.



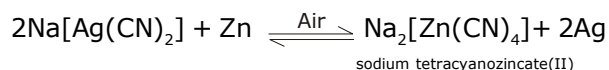
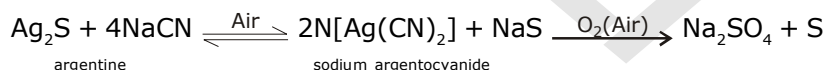
- (b) Many ligands (organic reagents) are used for the gravimetric estimation of number of metal ions.

Metal ion to be estimated	Cu^{2+}	Ni^{2+}	Fe^{3+}	Al^{3+}	Co^{2+}
Organic reagents used	Benzoin oxime	Dimethyl glyoxime	1,20-phenanthroline	8-hydroxy quinoline	α -nitroso β -naphthol

- (c) EDTA is used as a complexing agent in volumetric analysis of metal ions like Ca^{2+} , Mg^{2+} and Zn^{2+} .
- (d) The co-ordination compounds of the transition metals exhibit a variety of colours. This property is utilised in colorimetric analysis for the estimation of many metals.

(ii)

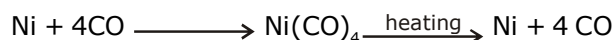
- (a) Metallurgical process : Silver and gold are extracted by the use of complex formation. Silver ore is treated with sodium cyanide solution with continuous passing of air through the solution. Silver dissolves as a cyanide complex and silver is precipitated by the addition of scrap zinc.



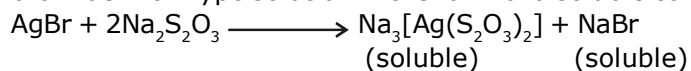
- (b) Native Gold and Silver also dissolve in NaCN solution in presence of the oxygen (air).



Silver and Gold are precipitated by addition of scrap zinc. Nickel is extracted by converting it into a volatile complex, nickel carbonyl, by use of carbon monoxide (Mond's process). The complex decomposes on heating again into pure nickel and carbon monoxide.



- (iii) **Photography** In photography, the image on the negative is fixed by dissolving all the remaining silver bromide with hypo solution in the form of a soluble complex.



- (iv) **Electroplating** Metal complexes release metal slowly and give a uniform coating of the metal on the desired object. Cyano complexes of silver, gold, copper and other metals are used for the electrodeposition of these metals.
- (v) **Biological processes** Metal complexes are of immense importance in biological processes. Haemoglobin, the red blood pigment, which acts as oxygen carrier to different parts of the body is a complex of iron (II). Vitamin B₁₂ is a complex of cobalt metal. The green colouring matter of plants, called chlorophyll, is a complex of magnesium. It acts as a catalyst in photosynthesis.

ORGANOMETALLIC COMPOUNDS

INTRODUCTION

Organometallic compounds are defined as those compounds in which the carbon atoms of organic (usually alkyl or aryl) groups are directly bonded to metal atoms. The compounds of elements such as boron, phosphorus, silicon, germanium and antimony with organic groups are also included in organometallics. Many organometallic compounds are important reagents which are used for the synthesis of organic compounds.

Classification of Organometallic Compounds

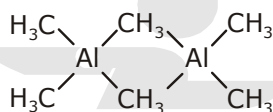
Organometallic compounds are classified in three classes.

(i) Sigma bonded organometallic compounds: In these complexes, the metal atom and carbon atom of the ligand are joined together with a sigma bond. For Examples:

(a) Grignard reagents, R – Mg – X where R is an alkyl or aryl group and X is a halogen.

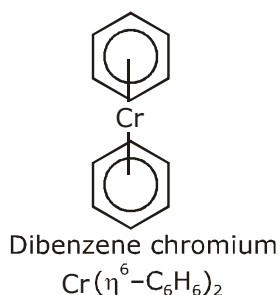
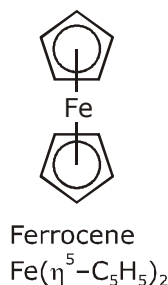
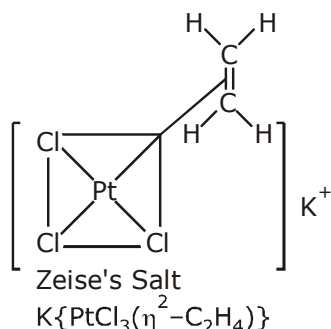
(b) Zinc compounds of the formula R₂Zn such as (C₂H₅)₂Zn. (isolated by Frankland).

Other similar compounds are (CH₃)₄Sn, (C₂H₅)₄Pb, Al₂(CH₃)₆, Al₂(C₂H₅)₆, Pb(CH₃)₄ etc.



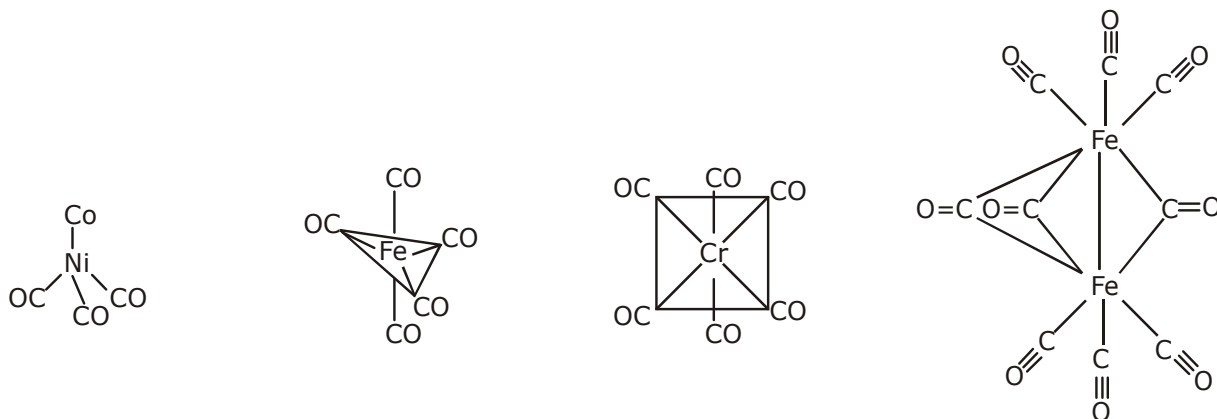
Al₂(CH₃)₆ is a dimeric compound and has a structure similar to diborane, (B₂H₆). It is an electron deficient compound and two methyl groups act as bridges between two aluminium atoms.

(ii) Pi-bonded organometallic compounds : These are the compounds of metals with alkenes, alkynes, benzene and other ring compounds. In these complexes, the metal and ligand form a bond that involves the π -electrons of the ligand. Three common examples are Zeise's salt, ferrocene and dibenzene chromium. These are shown below.

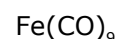
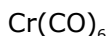
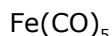
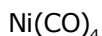


The number of carbon atoms bonded to the metal in these compounds is indicated by the greek letter η (eta) with a number. The prefixes η^2 , η^5 and η^6 indicate that 2, 5 and 6 carbon atoms are the metal in the compound.

- (iii) **Sigma and Pi bonded organometallic compounds :** Metal carbonyl compounds formed between metal and carbon monoxide, belong to this class. These compounds possess both σ - and π -bonding. Generally oxidation state of metal atoms in these compounds is zero. Carbonyls may be mononuclear, bridged or polynuclear.



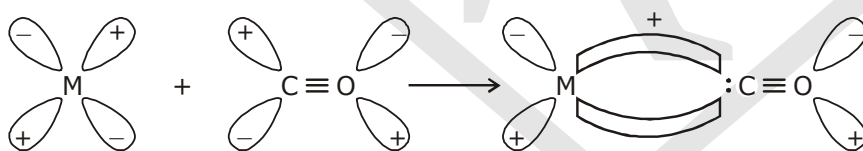
Tetracarbonyl nickel(0) Pentacarbonyl iron(0) Hexacarbonyl chromium(0)



In a metal carbonyl, the metal-carbon bond possesses both the σ - and π -character. A σ -bond between metal and carbon atom is formed when a vacant hybrid orbital of the metal atom overlap with an orbital on C atom of carbon monoxide containing a lone pair of electrons.



Formation of π -bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π^* orbital of C atom of carbon monoxide. This overlap is also called back donation of electrons by metal atom to carbon.



The π -overlap is perpendicular to the nodal plane of σ -bond.

In olefinic complexes, the bonding π -orbital electrons are donated to the empty orbital of the metal atom and at the same time to the back bonding p-orbital of the olefin.

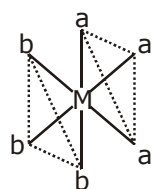
Applications of Organometallic Compounds

- Tetra ethyl lead (TEL) is used as antiknock compound in gasoline.
- Wilkinson's catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ is use as homogeneous catalyst in the hydrogenation of alkenes.
- The extraction and purification of nickel is based on the formation of organometallic compound Ni(CO)_4 . The formation of Ni(CO)_4 at $50\text{--}80^\circ\text{C}$ and its decomposition at $150\text{--}180^\circ\text{C}$ is used in the extraction of nickel by MONDS PROCESS.
- Zeigler Natta catalyst (trialkyl aluminium + titanium tetrachloride) acts as a heterogeneous catalyst in the polymerisation of ethylene in to polyethylene polymer.

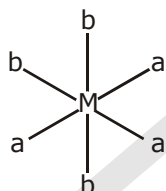
Points to be remembered:

- (i) $\text{CH}_3\text{B}(\text{OCH}_3)$ is an organometallic compound but $\text{B}(\text{OCH}_3)$ is not.
- (ii) The closed ring complexes formed by polydentate ligands are called Chelates. Chelation leads to stability.
- (iii) Estimation of nickel (II) is done by complexing with dimethyl glyoxime (DMG) whereas that of Ca^{+2} and Mg^{2+} ions is done by titrating against EDTA.
- (iv) Complex in which ligands can be substituted by other ligands are called labile complexes. For example $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is a labile complex because NH_3 ligands can be substituted by CN^- ligands.
- $$[\text{Cu}(\text{NH}_3)_4]^{2+} + 4 \text{CN}^- \rightarrow [\text{Cu}(\text{CN})_4]^{2-} + 4\text{NH}_3$$
- (less stable) (more stable)
- (v) Another type of geometrical isomerism is also shown by octahedral complexes of the type Ma_3b_3 .

if each trio of donor atoms occupy adjacent positions at the corner of an octahedral face, then it is called facial (fac) isomer and when the position are around the meridian of the octahedron, then it is called meridional (mer) isomer.



fac-form



Mer-form

- (vi) Haemoglobin is a complex of Fe, chlorophyll is a complex of Mg, vitamin B_{12} is a complex of Co.
- (vii) σ -bond organometallic compounds generally contains a non-transition metal linked to carbon atom of alkyl group by σ bond. For example eg. R-MgX .
- (viii) p -bonded organometallics are formed by donation of p -electrons of double bond to the metal atom. For example Zeise's salt $\text{K}[\text{PtCl}_3\eta^2\text{C}_2\text{H}_4]$ and Ferrocene $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2$
- (ix) Grignard's reagent is one of the most useful organometallic compounds. Due to the high polarity of ($\text{C}^{\delta-}\text{-Mg}^{\delta+}$) bond, it can be used to synthesise many organic compounds.

EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. The correct IUPAC name of the complex $\text{Fe}(\text{C}_5\text{H}_5)_2$ is –

(A) Cyclopentadienyl iron (II)
 (B) Bis (cyclopentadienyl) iron (II)
 (C) Dicyclopentadienyl ferrate (II)
 (D) Ferrocene

Sol.

2. Type of isomerism exhibited by $[\text{Cr}(\text{NCS})(\text{NH}_3)_5][\text{ZnCl}_4]$:

(A) Coordination isomerism
 (B) Linkage isomerism
 (C) Ionization isomerism
 (D) Both coordination and linkage isomerism

Sol.

3. Which complex ion has not tetrahedral geometry:

(A) $[\text{AgF}_4]^-$ (B) $[\text{HgI}_4]^{2-}$
 (C) $[\text{NiCl}_4]^{2-}$ (D) $[\text{Ni}(\text{CN})_4]^{4-}$

Sol.

4. Trioxalato aluminate (III) and tetrafluorido-borate (III) ions are respectively :

(A) $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$, $[\text{BF}_4]^{3-}$
 (B) $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3+}$, $[\text{BF}_4]^{3+}$
 (C) $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$, $[\text{BF}_4]^-$
 (D) $[\text{Al}(\text{C}_2\text{O}_4)_3]^{2-}$, $[\text{BF}_4]^{2-}$

Sol.

5. Which of the ligand can show linkage isomerism and acts as flexidentate ligand:

(A) CNS^- (B) NO_2^-
 (C) CN^- (D) NO_3^-

Sol.

6. Consider the following statements, "According to the Werner's theory. :

(1) Ligands are connected to the metal ions by covalent bonds.
 (2) Secondary valencies have directional properties.
 (3) Secondary valencies are non-ionisable.
 (4) Secondary valencies are satisfied by either neutral or negative legands.

Of these statements.

(A) 2, 3 and 4 are correct
 (B) 2 and 3 are correct
 (C) 1 and 3 are correct
 (D) 1, 2 and 4 are correct

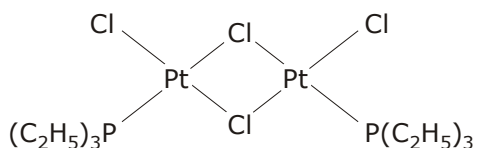
Sol.

7. From the stability constant (hypothetical values), given below, predict which is the strongest ligand:

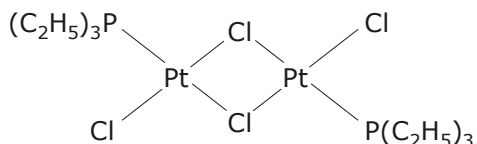
(A) $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$,
 $K = 4.5 \times 10^{11}$
 (B) $\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_4]^{2-}$,
 $K = 2.0 \times 10^{27}$
 (C) $\text{Cu}^{2+} + 2\text{en} \rightleftharpoons [\text{Cu}(\text{en})_2]^{2+}$,
 $K = 3.0 \times 10^{15}$
 (D) $\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$,
 $K = 9.5 \times 10^8$

Sol.

8. The complexes given below show:



and



- (A) Optical isomerism
(B) Co-ordination isomerism
(C) Geometrical isomerism
(D) Coordination position isomerism

Sol.

9. In which of the following complexes the nickel metal is in highest oxidation state.

- (A) $\text{Ni}(\text{CO})_4$
(B) $[\text{Cr}(\text{NH}_3)_6]_2[\text{NiF}_6]_3$
(C) $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$
(D) $\text{K}_4[\text{Ni}(\text{CN})_6]$

Sol.

10. An ion M^{2+} , forms the complexes $[\text{M}(\text{H}_2\text{O})_6]^{2+}$, $[\text{M}(\text{en})_3]^{2+}$ and $[\text{MBr}_6]^{4-}$, match the complex with the appropriate colour.

- (A) Green, blue and red
(B) Blue, red and green
(C) Green, red and blue
(D) Red, blue and green

Sol.

11. For the complex ion dichlorido bis (ethylene diamine) cobalt (III), select the correct statement.

- (A) It has three isomers, two of them are optically active and one is optically inactive.
(B) It has three isomers, all of them are optically active.
(C) It has three isomers, all of them are optically inactive.
(D) It has one optically active isomer and two geometrical isomers.

Sol.

12. $\text{Co}(\text{CO})_4$ follows EAN rule by :

- (A) Oxidizing character (B) Reduction
(C) Dimerization (D) All of these

Sol.

13. Type of isomerism exhibited by $[\text{Ir}(\text{OCN})_2(\text{H}_2\text{O})_3]$

- (A) Hydrate isomerism
(B) Linkage isomerism
(C) Polymerization isomerism
(D) Both (B) and (C)

Sol.

14. Which of the following complex exhibits geometrical isomerism:

- (A) $[\text{Zn}(\text{gly})_2]$ (B) $[\text{Cu}(\text{en})(\text{NH}_3)_2]^+$
(C) $[\text{PtBrCl}(\text{NH}_3)(\text{py})]$ (D) $[\text{Ni}(\text{CN})_2(\text{CO})_2]^{2-}$

Sol.

15. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is :

(A) $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_4$ (B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$
 (C) $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$ (D) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$

Sol.

16. The total number of possible isomers of the compound $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{II}}\text{Cl}_4]$ are :

(A) 3 (B) 5
 (C) 4 (D) 6

Sol.

17. In the complex $\text{Fe}(\text{CO})_x$, the value of x is :

(A) 3 (B) 4
 (C) 5 (D) 6

Sol.

18. The complex which exhibits cis-trans isomerism as well as can be resolved into d and ℓ forms:

(A) $[\text{Be}(\text{acac})_2]$ (B) $[\text{Ir}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{3+}$
 (C) $[\text{Cr}(\text{en})_3]^{3+}$ (D) $[\text{Rh}(\text{H}_2\text{O})_2(\text{en})_2]^{3+}$

Sol.

19. The oxidation state of Mo in its oxo-complex species $[\text{Mo}_2\text{O}_4(\text{C}_2\text{H}_4)_2(\text{H}_2\text{O})_2]^{2-}$ is :

(A) +2 (B) +3
 (C) +4 (D) +5

Sol.

20. The hybridisation and unpaired electrons in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ion are :

(A) sp^3d^2 ; 4 (B) d^2sp^3 ; 3
 (C) d^2sp^3 ; 4 (D) sp^3d^2 ; 2

Sol.

21. In which complex is the transition metal in zero oxidation state:

(A) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$
 (C) $\text{H}[\text{Co}(\text{CO})_4]$ (D) $\text{K}_4[\text{Ni}(\text{CN})_4]$

Sol.

22. Formula of ferrocene is :

(A) $[\text{Fe}(\text{CN})_6]^{4-}$ (B) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
 (C) $[\text{Fe}(\text{CO})_5]$ (D) $[\text{Fe}(\text{C}_5\text{H}_5)_2]$

Sol.

23. The hybridisation of Co in $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is :

(A) d^2sp^3 (B) dsp^2
 (C) sp^3 (D) sp^3d^2

Sol.

24. Which of the following is π complex :
(A) Trimethyl aluminium (B) Ferrocene
(C) Diethyl zinc
(D) Nickel tetra carbonyl

Sol.

25. Which complex is likely to show optical activity
(A) $\text{Trans}[\text{CoCl}_2(\text{NH}_3)_4]^+$
(B) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
(C) $\text{Cis}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$
(D) $\text{Trans}[\text{Co}(\text{NH}_3)_2(\text{en})_2]^{3+}$

Sol.

26. Which one is the most likely structure of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ if $1/3$ of total chlorine of the compound is precipitated by adding AgNO_3 to its aqueous solution :
(A) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$
(B) $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot (\text{H}_2\text{O})_3$
(C) $[\text{CrCl}_2(\text{H}_2\text{O})_4] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$
(D) $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$

Sol.

27. The two compounds $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ and $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Cl}$ represent :
(A) Linkage isomerism
(B) Ionisation isomerism
(C) Co-ordination isomerism
(D) No isomerism

Sol.

28. The structure of iron pentacarbonyl is :
(A) Square pyramidal (B) Trigonal bipyramidal
(C) Square planar (D) None of these

Sol.

29. The EAN of platinum in potassium hexachloroplatinate (IV) is :
(A) 46 (B) 86
(C) 36 (D) 84

Sol.

30. Diethylene triamine is :
(A) Chelating agent (B) Polydentate ligand
(C) Tridentate ligand (D) All of these

Sol.

31. How many moles of AgCl would be obtained, when 100ml of 0.1M $\text{CoCl}_3(\text{NH}_3)_5$ is treated with excess of AgNO_3 ?
(A) 0.01 (B) 0.02
(C) 0.03 (D) None of these

Sol.

32. 0.001 mol of $\text{Co}(\text{NH}_3)_5(\text{NO}_3)(\text{SO}_4)$ was passed through a cation exchanger and the acid coming out of it required 20 ml of 0.1 M NaOH for neutralisation. Hence the complex is :
(A) $[\text{CoSO}_4(\text{NH}_3)_5]\text{NO}_3$ (B) $[\text{CoNO}_3(\text{NH}_3)_5]\text{SO}_4$
(C) $[\text{Co}(\text{NH}_3)_5]\text{SO}_4\text{NO}_3$ (D) None of these

Sol.

33. Which of the following is non-ionizable –
 (A) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ (B) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
 (C) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (D) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$

Sol.

34. Which of the following is not chelating agent?
 (A) Hydrazine (B) oxalato
 (C) glycinate (D) ethylene diamine

Sol.

35. Which of the following has five donor (coordinating) sites and can act as flexidentate ligand?
 (A) Triethylene tetramine
 (B) Ethylenediamine tetracetate ion
 (C) Ethylenediamine triacetate ion
 (D) Tetraethylene penta amine

Sol.

36. Among TiF_6^{2-} , CoF_6^{3-} , Cu_2Cl_2 and NiCl_4^{2-} the colourless species are :
 (A) CoF_6^{3-} and NiCl_4^{2-}
 (B) TiF_6^{2-} and CoF_6^{3-}
 (C) NiCl_4^{2-} and Cu_2Cl_2
 (D) TiF_6^{2-} and Cu_2Cl_2

Sol.

37. The IUPAC name of the red coloured complex $[\text{Fe}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2]$ obtained from the reaction of Fe^{2+} and dimethyl glyoxime :

- (A) bis (dimethyl glyoxime) ferrate (II)
 (B) bis (dimethyl glyoximate) iron (II)
 (C) bis (2, 3-butanediol dioximate) iron (II)
 (D) bis (2,3-butanedione dioximate) iron (II)

Sol.

38. The molar ionic conductances of the octahedral complexes.

- (I) $\text{PtCl}_4 \cdot 5\text{NH}_3$ (II) $\text{PtCl}_4 \cdot 4\text{NH}_3$
 (III) $\text{PtCl}_4 \cdot 3\text{NH}_3$ (IV) $\text{PtCl}_4 \cdot 2\text{NH}_3$
 (A) $\text{I} < \text{II} < \text{III} < \text{IV}$ (B) $\text{IV} < \text{III} < \text{II} < \text{I}$
 (C) $\text{III} < \text{IV} < \text{II} < \text{I}$ (D) $\text{IV} < \text{III} < \text{I} < \text{II}$

Sol.

39. On treatment of 10ml of 1M solution of the complex $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with excess of AgNO_3 , 4.305g of AgCl was obtained. The complex is

- (A) $[\text{CrCl}_3(\text{H}_2\text{O})_3] \cdot 3\text{H}_2\text{O}$
 (B) $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
 (C) $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 (D) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

Sol.

40. Which of the following species is not expected to be a ligand :

- (A) NO^+ (B) NH_4^+
 (C) $\text{NH}_2\text{-NH}_3^+$ (D) NO_2^+

Sol.

41. The number of donor sites in dimethyl glyoxime, glycinato, diethylene triamine and EDTA are respectively

(A) 2, 2, 3 and 4 (B) 2, 2, 3 and 6
(C) 2, 2, 2 and 6 (D) 2, 3, 3 and 6

Sol.

42. EAN of the central metal in the complexes $K_2[Ni(CN)_4]$, $[Cu(NH_3)_4]SO_4$ and $K_2[PtCl_6]$ are respectively.

(A) 36, 35, 86 (B) 34, 35, 84
(C) 34, 35, 86 (D) 34, 36, 86

Sol.

43. Which of the following pair of complexes have the same EAN of the central metal atoms/ions?

(A) $[Cu(NH_3)_4]SO_4$ and $K_3[Fe(CN)_6]$
(B) $K_4[Fe(CN)_6]$ and $[Co(NH_3)_6]Cl_3$
(C) $K_3[Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6]Cl(NO_2)_2$
(D) all

Sol.

44. The complex that violates the Sidgwick's rule of EAN is :

(A) Potassium ferrocyanide
(B) Hexamine cobalt (III) Chloride
(C) Tetramine copper (II) sulphate
(D) Potassium dichloridodioxalato cobaltate (III)

Sol.

45. The IUPAC name for the coordination compound $Ba[BrF_4]_2$ is :

(A) Barium tetrafluoridobromate (V)
(B) Barium tetrafluoridobromate (III)
(C) Barium bis (tetrafluoridobromate) (III)
(D) None of these

Sol.

46. The formula of the complex hydridotrimethoxidoborate (III) ion is :

(A) $[BH(OCH_3)_3]^{2-}$ (B) $[BH_2(OCH_3)_3]^{2-}$
(C) $[BH(OCH_3)_3]^-$ (D) $[BH(OCH_3)_3]^+$

Sol.

47. The complex ion which has no 'd' electrons in the central metal atom is;

(A) $[Co(NH_3)_6]^{3+}$ (B) $[Fe(CN)_6]^{3-}$
(C) $[Cr(H_2O)_6]^{3+}$ (D) $[MnO_4]^-$

Sol.

48. Oxidation number of Fe in violet coloured complex $Na_4[Fe(CN)_5(NOS)]$ is :

(A) 0 (B) 2
(C) 3 (D) 4

Sol.

49. Complexes $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]\text{Br}$ and $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ can be distinguished by :
- (A) conductance measurement
(B) using BaCl_2
(C) using AgNO_3
(D) All

Sol.

50. Amongst the following ions, which one has the highest paramagnetism?
- (A) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
(C) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

Sol.

51. $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{NH}_3)_4]^{2+}$ do not differ in :
- (A) Magnetic moment (B) Oxidation number of Ni
(C) Geometry (D) EAN

Sol.

52. Which of the following statements is not correct?
- (A) $\text{Ti}(\text{NO}_3)_4$ is a colourless compound.
(B) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ is a coloured compound.
(C) $\text{K}_3[\text{VF}_6]$ is a colourless compound.
(D) $[\text{Cu}(\text{NCCH}_3)_4]\text{BF}_4$ is a colourless compound.

Sol.

53. The geometry of $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ are :
- (A) both square planar
(B) tetrahedral and square planar
(C) both tetrahedral
(D) square planar and tetrahedral

Sol.

54. Of the following which is paramagnetic in nature?
- (A) $\text{H}_2[\text{PbCl}_6]$ (B) $[\text{NiF}_6]^{2-}$
(C) $[\text{AgF}_4]^-$ (D) MnO_4^{2-}

Sol.

55. The $[\text{Fe}(\text{CN})_6]^{3-}$ complex ion
- (A) exhibits planar geometry
(B) is diamagnetic
(C) should be very stable
(D) has 2 unpaired electrons

Sol.

56. 50ml of 0.2M Solution of a compound with empirical formula $\text{CoCl}_3 \cdot 4\text{NH}_3$ on treatment with excess of $\text{AgNO}_3(\text{aq})$ yields 1.435 g of AgCl . Ammonia is not removed by treatment with concentrated H_2SO_4 . The formula of the compound is :
- (A) $\text{CoCl}_3(\text{NH}_3)_4$ (B) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$
(C) $[\text{Co}(\text{NH}_3)_4]\text{Cl}_3$ (D) $[\text{CoCl}_3(\text{NH}_3)]\text{NH}_3$

Sol.

57. Which of the following has conductance approximately equal to that of CaCl_2 .
 (A) $\text{CoCl}_3 \cdot 6\text{NH}_3$ (B) $\text{CoCl}_3 \cdot 5\text{NH}_3$
 (C) $\text{CoCl}_3 \cdot 4\text{NH}_3$ (D) $\text{CoCl}_3 \cdot 3\text{NH}_3$

Sol.

58. Aqueous solution of FeSO_4 gives tests for both Fe^{2+} and SO_4^{2-} but after addition of excess of KCN, solution ceases to give test for Fe^{2+} . This is due to the formation of :
 (A) the double salt $\text{FeSO}_4 \cdot 2\text{KCN} \cdot 6\text{H}_2\text{O}$
 (B) $\text{Fe}(\text{CN})_3$
 (C) the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$
 (D) the complex ion $[\text{Fe}(\text{CN})_6]^{3-}$

Sol.

59. The values of 'x' in complex $\text{H}_x[\text{Co}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_x(\pi\text{-C}_5\text{H}_5)]^+$ are respectively
 (A) 1,1 (B) 2,3
 (C) 3,1 (D) 1,3

Sol.

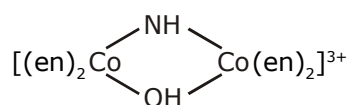
60. The number of sigma bond and equal Pt-Cl bond length in Zeise's salt is :
 (A) 6,2 (B) 6,3
 (C) 8,2 (D) 8,3

Sol.

61. The disodium salt of ethylene diamine tetracetic acid can be used to estimate the following ion(s) in the aqueous solution :
 (A) Mg^{2+} ion (B) Ca^{2+} ion
 (C) Na^+ ion (D) both Mg^{2+} and Ca^{2+}

Sol.

62. The oxidation number of Co in the complex ion



- (A) + 2 (B) + 3
 (C) + 4 (D) + 6

Sol.

63. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ has hybridisation and magnetic moment
 (A) sp^3 , 1.73 B. M. (B) sp^3d , 1.73 B. M.
 (C) dsp^2 , 2.83 B. M. (D) dsp^2 , 1.73 B. M.

Sol.

64. $[\text{FeF}_6]^{3-}$ has Fe atom ---- hybridised with unpaired -----electrons :
 (A) d^2sp^3 , 4 (B) d^2sp^3 , 5
 (C) sp^3d^2 , 5 (D) sp^3d^2 , 3

Sol.

65. Which of the following statements about $\text{Fe}(\text{CO})_5$ is correct?
 (A) It is paramagnetic and high spin complex
 (B) It is diamagnetic and high spin complex
 (C) It is diamagnetic and low spin complex
 (D) It is paramagnetic and low spin complex

Sol.

66. Which of the following statements is not true?
 (A) MnCl_4^{2-} ion has tetrahedral geometry and is paramagnetic
 (B) $[\text{Mn}(\text{CN})_6]^{2-}$ ion has octahedral geometry and is paramagnetic
 (C) $[\text{CuCl}_4]^{2-}$ has square planar geometry and is paramagnetic
 (D) $[\text{NiBr}_2(\text{Ph}_3\text{P})_3]$ has trigonal bipyramidal geometry and two unpaired electron

Sol.

67. Which of the following statements is incorrect?
 (A) Geometrical isomerism is not observed in complexes having tetrahedral geometry
 (B) Square planar complexes may show optical isomerism with ligands having chiral centre
 (C) Octahedral complexes having two chelating ligands in perpendicular plane always exhibit optical isomerism
 (D) Complex $[\text{Pt}(\text{Gly})_2]$ does not show geometrical isomerism

Sol.

68. Which of the following complex will give white precipitate with barium chloride solution –
 (A) $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ (B) $[\text{Cr}(\text{NH}_3)_4\text{SO}_4]\text{Cl}$
 (C) $[\text{Co}(\text{NH}_3)_6]\text{Br}_3$ (D) None of these

Sol.

69. $[\text{Co}(\text{en})_3]^{3+}$ ion is expected to show :
 (A) two optically active isomers; d and l forms.
 (B) three optically active isomers; d, l and meso forms.
 (C) four optically active isomers; cis, d and l isomers and trans d and l isomers.
 (D) None of these

Sol.

70. The number of geometrical isomers for octahedral $[\text{CoCl}_4(\text{NH}_3)_2]^-$, square planar $[\text{AuBr}_2\text{Cl}_2]^-$ and $[\text{PtCl}_2(\text{en})]$ are :
 (A) 2, 2, 2 (B) 2, 2, no isomerism
 (C) 3, 2, 2 (D) 2, 3, no isomerism

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)****One or More than One Option Correct**

1. Which of the following will produce a white precipitate upon reacting with AgNO_3 ?

(A) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (B) $[\text{Co}(\text{NH}_3)_3]\text{Cl}_3$
(C) $\text{K}_2[\text{Pt}(\text{en})_2\text{Cl}_2]$ (D) $[\text{Fe}(\text{en})_3]\text{Cl}_3$

Sol.

2. Which isomer of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is dark green in colour and forms one mole of AgCl with excess of AgNO_3 solution –

(A) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
(B) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
(C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$
(D) $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

Sol.

3. Which of the following are π -bonded organometallic compounds ?

(A) Ferrocene (B) $[\text{Ni}(\pi - \text{C}_5\text{H}_5)_2]$
(C) Ethylmagnesium iodide
(D) Dibenzene chromium

Sol.

4. Which of the following is /are inner orbital complex (es) as well as diamagnetic in nature.

(A) $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Ni}(\text{NH}_3)_6]^{2+}$
(C) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ (D) $[\text{Co}(\text{NH}_3)_6]^{3+}$

Sol.

5. Which of the following is /are correct about $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

(A) It is square planar complex
(B) It is paramagnetic with one unpaired electron in the d-subshell
(C) It gives white ppt with BaCl_2
(D) Its molar conductivity is approximately equal to that of $[\text{CrBr}(\text{NH}_3)_5]\text{SO}_4$

Sol.

6. Which of the following isomerism is /are shown by the complex $[\text{CoCl}_2(\text{OH})_2(\text{NH}_3)_2]\text{Br}$?

(A) Ionization (B) Linkage
(C) Geometrical (D) optical

Sol.

7. Both geometrical and optical isomerism are shown by

(A) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
(C) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (D) $[\text{Cr}(\text{OX})_3]^{3-}$

Sol.

8. Which of the following complexes have tetrahedral shape ?

(A) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (B) $[\text{Ni}(\text{CO})_4]$
(C) $[\text{NiCl}_4]^{2-}$ (D) $[\text{Zn}(\text{NH}_3)_4]^{2+}$

Sol.

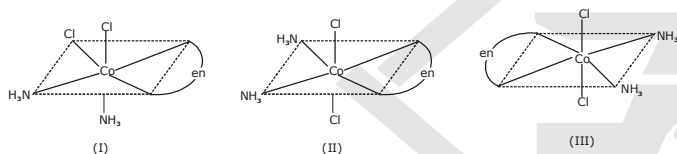
9. Which of the following is /are paramagnetic
 (A) $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Mn}(\text{CO})_5]^-$
 (C) $[\text{Fe}(\text{NH}_3)_6]^{2+}$ (D) $\text{Cr}_2\text{O}_7^{--}$

Sol.

10. Co-ordination number of Cr in $\text{CrCl}_3 \cdot 5\text{H}_2\text{O}$ is six. The volume of 0.1 N AgNO_3 needed to ppt. the chlorine in outer sphere in 200 ml of 0.01 M solution of the complex is /are :
 (A) 140 ml (B) 40 ml
 (C) 80 ml (D) 20 ml

Sol.

11. Three arrangement are shown for the complex $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$. Pick up the wrong statement.



- (A) I and II are geometrical isomers
 (B) II and III are optical isomers
 (C) I and III are optical isomers
 (D) II and III are geometrical isomers

Sol.

12. Which of the following statement (s) is (are) correct ?
 (A) hexacyanidoferrate (II) ion has four unpaired electrons in 3d-orbital
 (B) tetracyanidonickelate (II) ion is square planner
 (C) IUPAc name of $[\text{Zn}(\text{OH})_4]^{-2}$ ion is tetrahydroxidozine (II) ion
 (D) the coordination number of Cr in $[\text{Cr}(\text{NH}_3)_2(\text{en})_2]^{+3}$ is 6

Sol.

13. Correct statement is
 (A) $[\text{Co}(\text{ox})_3]^{3-}$ is more stable than $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (B) In $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ unpaired e^- lies in valence d and p orbital respectively
 (C) Colour due to d-d transition is found to be more intense than charge transfer spectra
 (D) δ -bond is found to be between metals in polynuclear metal carbonyl compounds

Sol.

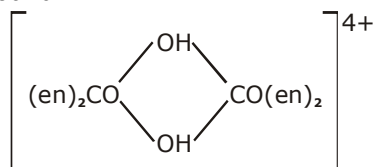
14. Which of the following statement(s) is (are) correct ?
 (A) The oxidation state of iron in sodium nitro prusside $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$ is +2
 (B) $[\text{Ag}(\text{NH}_3)_2]^+$ is linear in shape
 (C) In $[\text{Fe}(\text{H}_2\text{O})_6]^{+3}$, Fe is $d^2 sp^3$ hybridized
 (D) In $\text{Ni}(\text{CO})_4$, the oxidation state of Ni is zero

Sol.

15. Which of the following compound(s) show(s) optical isomerism
 (A) $[\text{Pt}(\text{bn})_2]^{2+}$
 (B) $[\text{CrCl}_2(\text{en})_2]^+$
 (C) $[\text{Co}(\text{en})_3][\text{CoF}_6]$
 (D) $[\text{Zn}(\text{gly})_2]^{2+}$

Sol.

16. Choose the correct IUPAC name(s) of the given compound



- (A) Bis(ethylenediamine) cobalt(III) di- μ -hydroxidobis(ethylenediamine)cobalt(III) ion
 (B) Di- μ -hydroxidotetrakis(ethylenediamine) dicobalt(III) ion
 (C) Di- μ hydroxidobis{bis(ethylenediamine)cobalt(III)}ion
 (D) Bis{ μ -hydroxidobis(ethylenediamine)cobalt(III)}ion

Sol.

17. Select incorrect statement(s) for $[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion.
 (A) Both $[\text{Cd}(\text{CN})_4]^{2-}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ have square planar geometry
 (B) $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ have equal no. of unpaired electron
 (C) $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cd}(\text{CN})_4]^{2-}$ can be separated from the mixture on passing H_2S gas
 (D) all the three complexes have magnetic moment equal to zero

Sol.

18. Which of the following statement is not true about the complex ion $[\text{CrCl}(\text{NO}_2)(\text{en})_2]^+$ (en = ethylene diamine)
 (A) It has two geometrical isomers-cis and trans
 (B) cis and trans forms are not diastereomers to each other
 (C) Only the cis isomer displays optical activity
 (D) It has three optically active isomers d, l and meso form

Sol.

19. Which of the following will have two stereoisomeric forms ?

- (A) $[\text{Cr}(\text{NO}_3)_3(\text{NH}_3)_3]$ (B) $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$
 (C) $[\text{CoCl}_2(\text{en})_2]^+$ (D) $[\text{CoBrCl}(\text{Ox})_2]^{3-}$

Sol.

20. Select the correct statement(s)
 (A) Co(III) is stabilised in presence of weak field ligands, while Co(II) is stabilised in presence of strong field ligand
 (B) Four coordinated complexes of Pd(II) and Pt(II) are diamagnetic and square planar
 (C) $[\text{Ni}(\text{CN})_4]^{4-}$ ion and $[\text{Ni}(\text{CO})_4]$ are diamagnetic tetrahedral complexes
 (D) Ni^{2+} ion does not form inner orbital octahedral complexes

Sol.

21. Which of the following names is/are correct for the compound $\text{Na}[\text{CoCl}_2(\text{NO}_2)(\sigma\text{-C}_3\text{H}_5)(\text{NH}_3)_2]$
 (A) Sodium allyldiamminedichloronitrito-N-cobaltate(III)
 (B) Sodium diamminedichloroallylnitrito-N-cobaltate(III)
 (C) Sodium diamminedichlorocyclopropylnitrito-N-cobaltate(III)
 (D) Sodium diamminecyclopropylnitrito-N-dichlorocobaltate(III)

Sol.

22. Which of the following compound(s) show(s) optical isomerism
 (A) $[\text{Pt}(\text{bn})_2]^{2+}$ (B) $[\text{CrCl}_2(\text{en})_2]^+$
 (C) $[\text{Co}(\text{en})_3]\text{CoF}_6]$ (D) $[\text{Zn}(\text{gly})_2]^{2+}$

Sol.

23. When AgNO_3 is added to a solution of $\text{Co}(\text{NH}_3)_5\text{Cl}_3$, the precipitate of AgCl shows two ionisable chloride ions.
 Select incorrect option(s)
 (A) Two chlorine atom satisfy primary valency and one secondary valency
 (B) One chlorine atom satisfies primary as well as secondary valency
 (C) Three chlorine atoms satisfy primary valency
 (D) Three chlorine atoms satisfy secondary valency

Sol.

COMPREHENSION TYPE

Comprehension Q. No. 24 to 26

When a transition metal ion (usually) is involved in octahedral complex formation, the five degenerate d-orbitals split into two set of degenerate orbitals (3 + 2). Three degenerate orbitals of lower energy (d_{xy} , d_{yz} , d_{zx}) and a set of degenerate orbitals of higher energy ($d_{x^2-y^2}$ and d_{z^2}). The orbitals with lower energy are called t_{2g} orbitals and those with higher energy are called e_g orbitals.

In octahedral complexes, positive metal ion may be considered to be present at the centre and negative ligands at the corner of a regular octahedron. As lobes of $d_{x^2-y^2}$ and d_{z^2} lie along the axes, i.e., along the ligands the repulsions are more and so high is the energy. The lobes of the remaining three d-orbitals lie between the axes. i.e., between the ligands. The repulsion between them are less, so lesser the energy. In the octahedral complexes, if metal ion has electrons more than 3 then for pairing them the option are

- (i) Pairing may start with 4th electron in t_{2g} orbitals.
 (ii) Pairing may start normally with 6th electrons when t_{2g} and e_g orbitals are singly filled.

24. In which of the following configuration hybridisation and magnetic moment of octahedral complexes are independent of nature of ligands.
 (i) d^3 configuration of any metal cation.
 (ii) d^6 configuration of IIIrd transition series metal cation.
 (iii) d^8 configuration of Ist transition series metal cation.
 (iv) d^7 configuration of any metal cation
 Select the correct code :

- (A) III, IV (B) I, III, IV
 (C) I, II, IV (D) I, II, III

Sol.

25. Which of the following electronic arrangement is /are possible for inner orbital oct complex.

- (I) $t_{2g}^3 e_g^2$ (II) $t_{2g}^6 e_g^1$

- (III) $t_{2g}^3 e_g^0$ (IV) $t_{2g}^4 e_g^2$

Select the correct code :

- (A) I, IV (B) II, III
 (C) III only (D) III, IV

Sol.

26. Select incorrect match for the following complexes.

- (A) $[\text{IrF}_6]^{3-}$ ($\Delta > P$)
 (B) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ ($\Delta < P$)
 (C) $\text{Fe}(\text{CO})_5$ ($\Delta > P$)
 (D) $[\text{PdCl}_2(\text{SCN})_2]^{2-}$ ($\Delta > P$)

Sol.

Comprehension Q. No. 27 to 29

$\text{Ni}(\text{NH}_3)_4(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ molecule may have two unpaired electron or zero unpaired electron and measurement of magnetic moment helps us to predict the geometry.

27. If magnetic moment value is zero then the formula of the complex will be
 (A) $[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
 (B) $[\text{Ni}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{NH}_3$
 (B) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 (D) $[\text{Ni}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$

Sol.

28. If the magnetic moment value is $2\sqrt{2}$ and conducts electricity then the formula of the complex is
 (A) $[\text{Ni}(\text{NH}_3)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
 (B) $[\text{Ni}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{NH}_3$
 (C) $[\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2$
 (D) $[\text{Ni}(\text{NH}_3)_4(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$

Sol.

29. The higher and lower value of magnetic moment of the given complex corresponds to the following geometries respectively.
 (A) Octahedron and tetrahedron
 (B) Octahedron and square planar
 (C) Square planar and octahedron
 (D) Octahedron and octahedron

Sol.

Comprehension Q. No. 30 to 32

The necessary and sufficient condition to exhibit optical activity, the configuration of the given complex should be asymmetric.

30. The complex ions $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ are called –
 (A) Ionization isomers
 (B) Linkage isomers
 (C) Coordination isomers
 (D) Hydrate isomers

Sol.

31. The complex which does not exhibit cis-trans isomersim but optically active
 (A) $[\text{Zn}(\text{gly})_2]$ (B) $[\text{Pt}(\text{gly})_2]$
 (C) $[\text{Ni}(\text{gly})_2]$ (D) $[\text{Pd}(\text{gly})_2]$

Sol.

32. The complex in which six pair of enantiomers available form is optically active
 (A) $[\text{CoBrCl}(\text{CN})(\text{H}_2\text{O})(\text{NH}_3)_2]$
 (B) $[\text{Rh}(\text{CN})_2(\text{gly})(\text{H}_2\text{O})(\text{NH}_3)]$
 (C) $[\text{FeF}_2(\text{OH})_2(\text{en})]^-$
 (D) $[\text{CrBr}_2\text{Cl}(\text{CN})(\text{NH}_3)_2]^-$

Sol.

Comprehension Q. No. 33 to 34

No single theory of bonding of complex compound is sufficient to describe the bonding, magnetic property, colour, etc of a given complex.

33. The tetrahedral complex which is diamagnetic but coloured.
 (A) $[\text{NiCl}_4]^{2-}$ (B) $[\text{CrO}_4]^{2-}$
 (C) $[\text{MnO}_4]^{2-}$ (D) $[\text{Cd}(\text{CN})_4]^{2-}$

Sol.

34. The incorrect statement about $\text{Ni}(\text{CO})_4$ is –
 (A) The bond order of CO in the complex is less than bond order of CO molecule.
 (B) The complex is diamagnetic and dsp^2 hybridised
 (C) The bond order of Ni – C bond is greater than one.
 (D) The complex cannot act as oxidizing or reducing agent according to sidwick EAN rule

Sol.

Match the Column :**35. Column - I**

- (A) $[\text{Ma}_2\text{bcde}]^{n\pm}$
 (B) $[\text{Ma}_2\text{b}_2\text{c}_2]^{n\pm}$
 (C) $[\text{M}(\text{AB})_2\text{C}_2\text{D}_2]^{n\pm}$

Column - II

- (P) 1 cis isomer
 (Q) 4 geometrical isomers
 (R) 5 stereo(space) isomers
 (S) 3 trans isomers

(where AB \rightarrow Unsym. bidentate ligand, a,b,c,d & e \rightarrow monodentate ligands)

Sol.

36. Column - I

- (A) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$
 (B) $[\text{Co}(\text{CN})_2(\text{NH}_3)_4]\text{OC}_2\text{H}_5$
 (C) $[\text{IrCl}_6]^{3-}$
 (D) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$

Column - II

- (P) d^2sp^3 hybridisation
 (Q) Ionisation isomerism
 (R) $\mu = 2.83$ B.M.
 (S) $\Delta_0 < P$

Sol.

37. Column - I

- (A) $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 (B) $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$
 (C) $\text{K}_4[\text{Fe}(\text{CN})_6]$
 (D) $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_3$

Column - II

- (P) dsp^2
 (Q) Octahedral
 (R) sp^3d^2
 (S) square planar

Sol.

38. Column - I (Complex)

- (A) $[\text{Co}(\text{en})_3]^{2+}$
 (B) $[\text{Ca}(\text{EDTA})]^{2-}$
 (C) $[\text{Ni}(\text{CO})_4]$
 (D) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

Column - II (C.N)

- (P) 6
 (Q) 4
 (R) 2
 (S) 5

Sol.

39. Column - I (Complexes)

- (A) $[\text{CoCl}_3(\text{NH}_3)_3]$
 (B) $[\text{Cr}(\text{OX})_3]^{3-}$
 (C) $[\text{CrCl}_2(\text{OX})_2]$
 (D) $[\text{RhCl}_3(\text{Py})_3]$

Column - II (Stereoproperties)

- (P) Show facial isomer
 (Q) Cis form is optically active
 (R) Trans form is optically active
 (S) Show meridional form
 (T) Two optically active isomer

Sol.

40. Column - I

- (A) $[\text{Fe}(\text{CO})_4]^{2-}$
 (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 (C) $\text{K}_2[\text{Ni}(\text{CN})_4]$
 (D) $[\text{Cu}(\text{NH}_3)_4]^{2+}$

Sol.

Column - II

- (P) 34
 (Q) 35
 (R) 36
 (S) 37

41. Column - I

- (A) $[\text{Fe}(\text{NH}_3)_6]^{2+}$
 (B) $[\text{NiF}_6]^{2-}$
 (C) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (D) $[\text{Pt}(\text{Cl}_2)(\text{NH}_3)_4]\text{Cl}_2$

Sol.

Column - II

- (P) d^2sp^3
 (Q) sp^3d^2
 (R) diamagnetic
 (S) Paramagnetic
 (T) outer orbital complex

42. Column - I

- (A) $[\text{MnCl}_6]^{2-}$
 (B) $[\text{Fe}(\text{CN})_6]^{3-}$
 (C) $[\text{CoF}_6]^{3-}$
 (D) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Sol.

Column - II

- (P) One unpaired electron
 (Q) d^2sp^3
 (R) sp^3d^2
 (S) Four unpaired electron

43. Column - I

- (A) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (B) $[\text{CuCl}_4]^{2-}$
 (C) $\text{K}_2[\text{Cr}(\text{CN})_4(\text{NH}_3)(\text{NO}^+)]$
 (D) $\text{K}_4[\text{CO}(\text{NO}_2)_6]$

Column - II

- (P) Inner orbital complex
 (Q) Magnetic moment = 1.73 B.M.
 (R) Metal oxidation state + 2
 (S) During hybridisation d-orbital electron is transferred to higher energy orbital

Sol.

44. Column - I

- (A) Only four stereoisomer
 (B) Four optically active isomer
 (C) Double the number of geometrical isomer compared to any other complex given in column II.

Sol.

Column - II

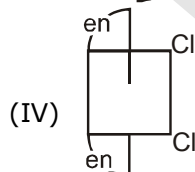
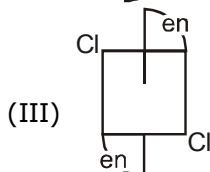
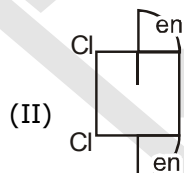
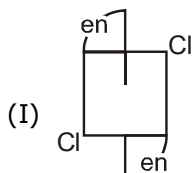
- (P) $[\text{M}(\text{AB})_3]^{n\pm}$
 (Q) $[\text{M}(\text{AA})_2\text{a}_2\text{b}_2]^{n\pm}$
 (R) $[\text{M} \text{a}_2\text{b}_2 \text{cd}]^{n\pm}$
 (S) $[\text{Ma}_3\text{bcd}]^{n\pm}$

EXERCISE – III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Which of the following statements is not true about the complex ion $[\text{CrCl}_2(\text{en})_2]^+$:
- (A) It has two geometrical isomers – cis and trans.
 (B) Both the cis and trans isomers display optical activity.
 (C) Only the cis isomer displays optical activity.
 (D) Only the cis isomer has non-superimposable mirror image.

Sol.

2. Of the following configurations, the optical active isomers are :

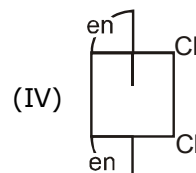
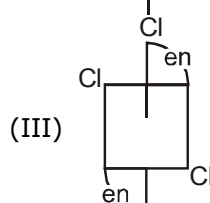
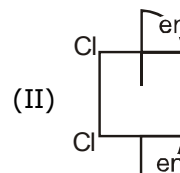
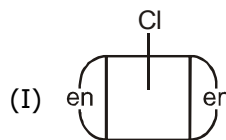


- (A) I and II
 (C) II and IV

- (B) I and III
 (D) II and III

Sol.

3. Identify the geometrical isomers of the following



- (A) I with III
 (C) I with II & IV

- (B) II with IV
 (D) none of these

Sol.

4. Other than the X-ray diffractions, how could be the following pairs of isomers be distinguished from one another by :

$[\text{Cr}(\text{NH}_3)_6]$ $[\text{Cr}(\text{NO}_2)_6]$ and $[\text{Cr}(\text{NO}_2)_2(\text{NH}_3)_4]$
 $[\text{Cr}(\text{NO}_2)_4(\text{NH}_3)_2]$

- (A) electrolysis of an aqueous solution
 (B) measurement of molar conductance
 (C) measuring magnetic moments
 (D) observing their colours

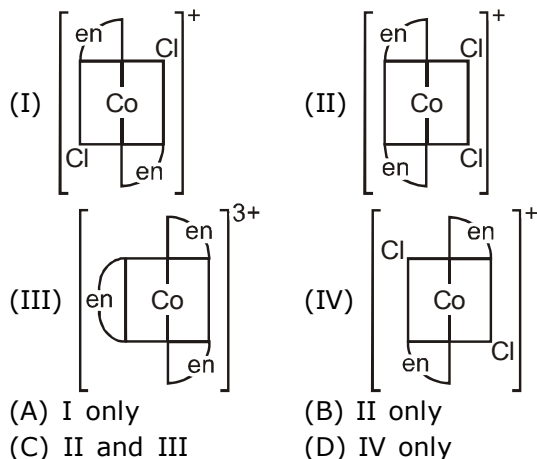
Sol.

5. How the isomeric complexes $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{NO}_2)_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ can be distinguished from one another by

- (A) Conductivity measurement
 (B) Measuring magnetic moments
 (C) Electrolysis of their aqueous solutions
 (D) Optical measurement

Sol.

6. Which of the following ions are optically active?

**Sol.**

7. Octahedral complex of Ni(II) will be always:
 (A) inner orbital (B) outer orbital
 (C) inner or outer orbital depending upon the strong or weak field ligand
 (D) none of these

Sol.

8. For the correct assignment of electronic configuration of a complex, the valence bond theory often required the measurement of :
 (A) molar conductance (B) optical activity
 (C) magnetic moment (D) dipole moment

Sol.

9. Mn^{2+} forms a complex with Br^- ion. The magnetic moment of the complex is 5.92 B. M. What could not be the probable formula and geometry of the complex?

(A) $[\text{MnBr}_6]^{4-}$, octahedral
 (B) $[\text{MnBr}_4]^{2-}$, square planar
 (C) $[\text{MnBr}_4]^{2-}$, tetrahedral
 (D) $[\text{MnBr}_5]^{3-}$, trigonal bipyramidal

Sol.

10. How many isomers are possible for the complex ion $[\text{CrCl}_3(\text{OH})_2(\text{NH}_3)]^{2-}$

(A) 2 (B) 3
 (C) 4 (D) 5

Sol.

11. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be :

(A) Co^{2+} (B) Mn^{2+}
 (C) Fe^{2+} (D) Fe^{3+}

Sol.

12. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{PdBr}_4]^{2-}$ complex ions are respectively :

(A) low spin, high spin
 (B) high spin, low spin
 (C) both low spin
 (D) both high spin

Sol.

13. Ethylenediaminetetraacetic acid (EDTA) is the antidote for lead poisoning. It is administered in the form of

- (A) free acid
(B) sodium dihydrogen salt
(C) Calcium dihydrogen salt
(D) None of these

Sol.

14. The species having tetrahedral shape is

- (A) $[\text{PdCl}_4]^{2-}$ (B) $[\text{Ni}(\text{CN})_4]^{2-}$
(C) $[\text{Pd}(\text{CN})_4]^{2-}$ (D) $[\text{NiCl}_4]^{2-}$

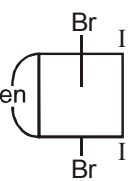
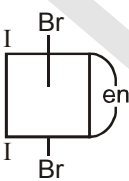
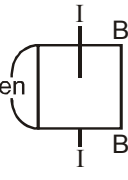
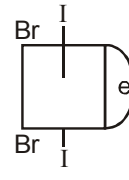
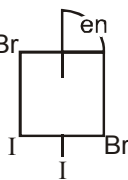
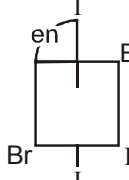
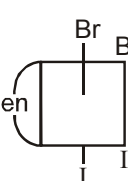
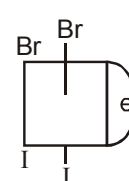
Sol.

15. Which one of the following species does not represent cationic species of vanadium formed in aqueous solution :

- (A) VO_2^+ (B) VO^{2+}
(C) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (D) VO_2^{2+}

Sol.

16. The complex ion has two optical isomers. Their correct configurations are :

- (A)  and 
(B)  and 
(C)  and 
(D)  and 

Sol.

17. The EAN of metal atoms in $\text{Fe}(\text{CO})_2(\text{NO})_2$ and $\text{Co}_2(\text{CO})_8$ respectively are :

- (A) 34, 35 (B) 34, 36
(C) 36, 36 (D) 36, 35

Sol.

18. Following Sidgwick's rule of EAN, $\text{Co}_2(\text{CO})_x$ will be :

- (A) $\text{Co}_2(\text{CO})_4$ (B) $\text{Co}_2(\text{CO})_3$
(C) $\text{Co}_2(\text{CO})_8$ (D) $\text{Co}_2(\text{CO})_{10}$

Sol.

19. On treatment of $[\text{Ni}(\text{NH}_3)_4]^{2+}$ with concentrated HCl, two compounds I and II having the same formula, $[\text{NiCl}_2(\text{NH}_3)_2]$ are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalic acid to form $[\text{Ni}(\text{C}_2\text{O}_4)(\text{NH}_3)_2]$ whereas II does not react. Point out the correct statement of the following

- (A) I cis, II trans; both tetrahedral
(B) I cis, II trans; both square planar
(C) I trans, II cis; both tetrahedral
(D) I trans, II cis; both square planar

Sol.

20. Which one of the following statement is incorrect?

- (A) Greater the formation constant (K_f) of a complex ion, greater is its stability.
- (B) Greater the positive charge on the central metal ion, greater is the stability of the complex.
- (C) Greater is the basic character of the ligand, lesser is the stability of the complex.
- (D) Chelate complexes have high stability constants.

Sol.

21. Point out the correct statements amongst the following :

- (A) $[\text{Cu}(\text{CN})_4]^{3-}$ has tetrahedral geometry and dsp^2 hybridization.
- (B) $[\text{Ni}(\text{CN})_6]^{4-}$ is octahedral and Ni has d^2sp^2 hybridization.
- (C) $[\text{ZnBr}_4]^{2-}$ is tetrahedral and diamagnetic.
- (D) $[\text{Cr}(\text{NH}_3)_6]^{3+}$ has octahedral geometry and sp^3d^2 hybridization.

Sol.

22. Among the following ions which one has the highest paramagnetism :

- (A) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
- (C) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (D) $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$

Sol.

23. Among the following, the compound that is both paramagnetic and coloured is :

- (A) $\text{K}_2\text{Cr}_2\text{O}_7$ (B) $(\text{NH}_4)_2[\text{TiCl}_6]$
- (C) VOSO_4 (D) $\text{K}_3[\text{Cu}(\text{CN})_4]$

Sol.

24. In the isoelectronic series of metal carbonyl, the CO bond strength is expected to increase in the order.

- (A) $[\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6] < [\text{V}(\text{CO})_6]^-$
- (B) $[\text{V}(\text{CO})_6]^- < [\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+$
- (C) $[\text{V}(\text{CO})_6]^- < [\text{Mn}(\text{CO})_6]^+ < [\text{Cr}(\text{CO})_6]$
- (D) $[\text{Cr}(\text{CO})_6] < [\text{Mn}(\text{CO})_6]^+ < [\text{V}(\text{CO})_6]^-$

Sol.

25. Which compound is formed when excess of KCN is added to aqueous solution of copper sulphate?

- (A) $\text{Cu}(\text{CN})_2$ (B) $\text{K}_2[\text{Cu}(\text{CN})_4]$
- (C) $\text{K}[\text{Cu}(\text{CN})_2]$ (D) $\text{K}_3[\text{Cu}(\text{CN})_4]$

Sol.

26. Which of the following complex shows ionization isomerism :

- (A) $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (B) $[\text{Cr}(\text{en})_2]\text{Cl}_2$
- (C) $[\text{Cr}(\text{en})_3]\text{Cl}_3$ (D) $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$

Sol.

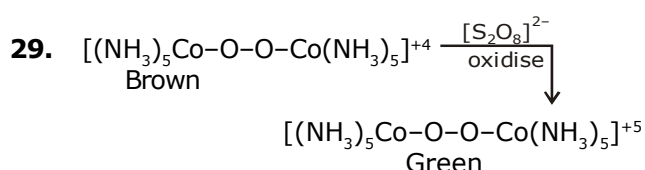
27. Which of the following statements are true/false-

- (i) $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ (ii) $[\text{CoCl}_4]^{2-}$
- (iii) $[\text{Co}(\text{dmg})_2]$
- (a) i, ii are paramagnetic & iii is diamagnetic in nature
- (b) i & ii has magnetic moment greater than iii
- (c) i, ii has tetrahedral structure and iii has square planar structure
- (d) In i, ii there is one unpaired electron and in iii it has 3 unpaired electrons
- (A) FTFT (B) FFTT
- (C) TFTF (D) FTTF

Sol.

28. If NO reacts with $[\text{Cr}(\text{CO})_6]$ how many CO groups can be replaced by NO :
 (A) All the 6 CO groups are replaced by 6 NO groups
 (B) All the 4 CO groups are replaced by 6 NO groups
 (C) All the 2 CO groups are replaced by 3 NO groups
 (D) All the 6 CO groups are replaced by 4 NO groups

Sol.



The magnetic moment of green complex is 1.7 BM & for brown complexes magnetic moment is zero.

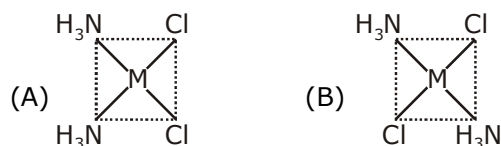
(O-O) is same in all respect in both the complexes.

The O. S. of Co in brown complex & green complex respectively are-

- (A) III III & IV III
brown green
 (B) III II & III III
brown green
 (C) III III & III II
brown green
 (D) III IV & III III
brown green

Sol.

30. Which of the following isomers of $[\text{M}(\text{NH}_3)_2\text{Cl}_2]$ would react with potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4$):



- (C) Both (D) None

Sol.

31. The complex $\text{K}_4[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$ is oxidised into $\text{K}_2[\text{Zn}(\text{CN})_4(\text{O}_2)_2]$, then which of the following is/are correct?

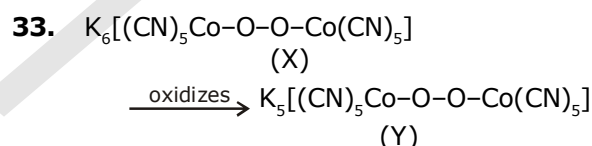
- (A) Zn(II) is oxidised into Zn (IV)
 (B) Paramagnetic moment decreases
 (C) O - O bond length increases
 (D) Paramagnetic moment increase

Sol.

32. All the following complexes show decrease in their weight when placed in a magnetic balance then the group of complexes having tetrahedral geometry is :

- (I) $\text{Ni}(\text{CO})_4$ (II) $\text{K}[\text{AgF}_4]$
 (III) $\text{Na}_2[\text{Zn}(\text{CN})_4]$ (V) $[\text{RhCl}(\text{PPh}_3)_3]$
 (IV) $\text{K}_2[\text{PtCl}_4]$ (B) I, II, III
 (A) II, III, V (D) None of these
 (C) I, III, IV

Sol.



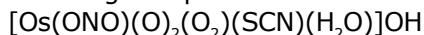
In both the complexes Co cation have $t_{2g}^6 e_g^0$ configuration.

The B. E. of (O-O) in X & Y is

- (A) B. E. of (O - O) in Y < B. E. of (O - O) in X
 (B) B. E. of (O - O) in X < B. E. of (O - O) in Y
 (C) B. E. of (O - O) in X = B. E. of (O - O) in Y
 (D) can't be compared

Sol.

- 34.** What is oxidation state, magnetic moment and type of hybridisation of central metal cation in following complex.



- (A) +7, $\sqrt{3}$ B. M., d^2sp^3 hybridisation
 (B) +8, 0 B. M., sp^3d^2 hybridisation
 (C) +8, 0 B. M., d^2sp^3 hybridisation
 (D) +9, 0 B. M., sp^3d^2 hybridisation

Sol.

- 35.** Which of the following option is having maximum number of unpaired electrons.

- (A) A tetrahedral d^6 ion
 (B) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (C) A square planar d^7 ion
 (D) A co-ordination compound with magnetic moment of 5.92 B.M.

Sol.

- 36.** Which one of the following octahedral complexes will not show geometrical isomerism (A and B are monodentate ligands) –

- (A) $[\text{MA}_5\text{B}]$ (B) $[\text{MA}_2\text{B}_4]$
 (C) $[\text{MA}_3\text{B}_3]$ (D) $[\text{MA}_4\text{B}_2]$

Sol.

- 37.** The number of possible isomers by the compounds like $[\text{Cd}(\text{gly})_2]$ and $[\text{Pd}(\text{gly})_2]$ are respectively.

- (A) 0, 2 (B) 1, 2
 (C) 2, 2 (D) 1, 1

Sol.

- 38.** Which of the following complexes is diamagnetic?
 (A) $[\text{Fe}(\text{CN})_6]^{4-}$ (B) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (C) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (D) $[\text{Fe}(\text{CN})_6]^{3-}$

Sol.

- 39.** For the $t_{2g}^6 e_g^2$ system, the value of magnetic moment (m) is –

- (A) 2.83 B.M. (B) 1.73 B.M.
 (C) 3.87 B.M. (D) 4.92 B.M.

Sol.

- 40.** The magnetic moment of a complex ion is 2.83 BM. The complex ion is

- (A) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Cu}(\text{CN})_4]^{3-}$
 (C) $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ (D) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

Sol.

- 41.** The complex having highest Δ value

- (A) $[\text{Ni}(\text{en})_3]^{2+}$ (B) $[\text{Ni}(\text{CN})_4]^{2-}$
 (C) $[\text{NiCl}_4]^{2-}$ (D) $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Sol.

- 42.** Which of the following complex is with lowest number of unpaired electron

- (A) $[\text{NiF}_6]^{2-}$ (B) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (C) $[\text{CoF}_6]^{3-}$ (D) $[\text{Fe}(\text{EDTA})]^-$

Sol.

EXERCISE – IV**PREVIOUS YEARS****LEVEL – I****JEE MAIN****OBJECTIVE**

Q.1 In $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, the isomerism shown is
[AIEEE-2002]

- (A) Ligand (B) Optical
(C) Geometrical (D) Ionization

Sol.

Q.2 In the complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3+}$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{FeCl}_6]^{3-}$, more stability is shown by –
[AIEEE-2002]

- (A) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (B) $[\text{Fe}(\text{CN})_6]^{3+}$
(C) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ (D) $[\text{FeCl}_6]^{3-}$

Sol.

Q.3 One mole of the complex compound $\text{Co}(\text{NH}_3)_5\text{Cl}_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of AgNO_3 solution to yield two moles of $\text{AgCl}(\text{s})$. The structure of the complex is –
[AIEEE-2003]

- (A) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] \cdot 2\text{NH}_3$
(B) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{Cl} \cdot \text{NH}_3$
(C) $[\text{Co}(\text{NH}_3)_4\text{Cl}] \text{Cl}_2 \cdot \text{NH}_3$
(D) $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Cl}_2$

Sol.

Q.4 In the coordination compound $\text{K}_4[\text{Ni}(\text{CN})_4]$, the oxidation state of nickel is – [AIEEE-2003]

- (A) 0 (B) +1
(C) +2 (D) -1

Sol.

Q.5 The number of 3d-electrons remained in Fe^{2+} (At. no. of Fe = 26) is –
[AIEEE-2003]

- (A) 4 (B) 5
(C) 6 (D) 3

Sol.

Q.6 Ammonia forms the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion with copper ions in alkaline solutions but not in acidic solution. What is the reason for it –
[AIEEE-2003]

- (A) In acidic solution hydration protects copper ions
(B) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available
(C) In alkaline solutions insoluble $\text{Cu}(\text{OH})_2$ is precipitated which is soluble in excess of any alkali
(D) Copper hydroxide is an amphoteric substance

Sol.

Q.7 Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is –
[AIEEE-2004]

- (A) c, a (B) b, c
(C) a, b (D) a, b, c

Sol.

Q.8 The coordination number of a central metal atom in a complex is determined by –
[AIEEE-2004]

- (A) The number of ligands around a metal ion bonded by sigma and pi-bonds both
(B) The number of ligands around a metal ion bonded by pi-bonds
(C) The number of ligands around a metal ion bonded by coordinate bonds
(D) The number of only anionic ligands bonded to the metal ion

Sol.

Q.9 Which one of the following complexes in an outer orbitals complex – **[AIEEE-2004]**

- (A) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (B) $[\text{Mn}(\text{CN})_6]^{4-}$
(C) $[\text{Fe}(\text{CN})_6]^{4-}$ (D) $[\text{Ni}(\text{NH}_3)_6]^{2+}$

(Atomic nos. : Mn = 25; Fe = 26; Co = 27; Ni = 28)

Sol.

Q.10 Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect ? **[AIEEE-2004]**

- (A) Cyanocobalamin is vitamin B₁₂ and contains cobalt
(B) Haemoglobin is the red pigment of blood and contains iron
(C) Chlorophylls are green pigments in plants and contain calcium
(D) Carboxypeptidase-A is an enzyme and contains zinc

Sol.

Q.11 The correct order of magnetic moments (spin only values in B.M. among is) – **[AIEEE-2004]**

- (A) $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$
(B) $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$
(C) $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$
(D) $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$

(Atomic nos : Mn = 25 ; Fe = 26 ; Co = 27 ; Ni = 28)

Sol.

Q.12 The value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM . The correct one is – **[AIEEE-2005]**

- (A) d^4 (in strong ligand field)
(B) d^4 (in weak ligand field)
(C) d^3 (in weak as well as in strong field)
(D) d^5 (in strong ligand field)

Sol.

Q.13 The IUPAC name for the complex $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ is – **[AIEEE-2006]**

- (A) pentaammine nitrito-N-cobalt (II) chloride
(B) pentaammine nitrito-N-cobalt (III) chloride
(C) nitrito-N-pentaamminecobalt (III) chloride
(D) nitrito-N-pentaamminecobalt (II) chloride

Sol.

Q.14 Nickel (Z = 28) combines with a ninegative monodentate ligand X^- to form a paramagnetic complex $[\text{NiX}_4]^{2-}$. The number of unpaired electron in the nickel and geometry of this complex ion are respectively – **[AIEEE-2006]**

- (A) one, square planar
(B) two, square planar
(C) one, tetrahedral (D) two, tetrahedral

Sol.

Q.15 In $\text{Fe}(\text{CO})_5$, the Fe–C bond possesses – **[AIEEE-2006]**

- (A) ionic character
(B) σ -character only
(C) π -character
(D) both σ and π character

Sol.

Q.16 How many EDTA (ethylenediaminetetraacetate ion) molecules are required to make an octahedral complex with a Ca^{2+} ion ?

[AIEEE-2006]

- (A) One (B) Two
(C) Six (D) Three

Sol.

Q.17 The "spin-only" magnetic moment [in units of Bohr magneton] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28) – [AIEEE-2006]

- (A) 0 (B) 1.73
(C) 2.84 (D) 4.90

Sol.

Q.18 Which one of the following has a square planar geometry - (Co = 27, Ni = 28, Fe = 26, Pt = 78) –

[AIEEE-2007]

- (A) $[\text{CoCl}_4]^{2-}$ (B) $[\text{FeCl}_4]^{2-}$
(C) $[\text{NiCl}_4]^{2-}$ (D) $[\text{PtCl}_4]^{2-}$

Sol.

Q.19 The coordination number and the oxidation state of the element 'E' in the complex $[\text{E}(\text{en})_2(\text{C}_2\text{O}_4)] \text{NO}_2$ (where (en) is ethylene diamine) are, respectively – [AIEEE-2008]

- (A) 6 and +2 (B) 4 and +2
(C) 4 and +3 (D) 6 and +3

Sol.

Q.20 In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of Δ_0 be the highest ?

- (A) $[\text{Co}(\text{CN})_6]^{3-}$ (B) $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
(C) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (D) $[\text{Co}(\text{NH}_3)_6]^{3+}$

Sol.

Q.21 Which of the following has an optical isomer ? [AIEEE-2009]

- (A) $[\text{Co}(\text{en})(\text{NH}_3)_2]^{2+}$
(B) $[\text{Co}(\text{H}_2\text{O})_4(\text{en})]^{3+}$
(C) $[\text{Co}(\text{en})_2(\text{NH}_3)_2]^{3+}$
(D) $[\text{Co}(\text{NH}_3)_3\text{Cl}]^+$

Sol.

Q.22 Which of the following pairs represents linkage isomers ? [AIEEE-2009]

- (A) $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$ and $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
(B) $[\text{Co}(\text{NH}_3)_5\text{NO}_3] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{NO}_3$
(C) $[\text{PtCl}_2(\text{NH}_3)_4] \text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4] \text{Cl}_2$
(D) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$

Sol.

LEVEL – II

JEE ADVANCED

OBJECTIVE

1. The pair of compounds having metals in their highest oxidation state is **[JEE-2004]**

(A) MnO_2 , FeCl_3
 (B) $[\text{MnO}_4]^-$, CrO_2Cl_2
 (C) $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_3]$
 (D) $[\text{NiCl}_4]^{2-}$, $[\text{CoCl}_4]^-$

Sol.

2. The compound having tetrahedral geometry is **[JEE-2004]**

(A) $[\text{Ni}(\text{CN})_4]^{2-}$ (B) $[\text{Pd}(\text{CN})_4]^{2-}$
 (C) $[\text{PdCl}_4]^{2-}$ (D) $[\text{NiCl}_4]^{2-}$

Sol.

3. Spin only magnetic moment of the compound $\text{Hg}[\text{Co}(\text{SCN})_4]$ is **[JEE-2004]**

(A) $\sqrt{3}$ (B) $\sqrt{15}$
 (C) $\sqrt{24}$ (D) $\sqrt{8}$

Sol.

4. Which of the following pair is expected to exhibit same colour in solution ? **[JEE-2005]**

(A) VOCl_2 ; FeCl_2 (B) CuCl_2 ; VOCl_2
 (C) MnCl_2 ; FeCl_2 (D) FeCl_2 ; CuCl_2

Sol.

5. Which type of isomerism is shown by $[\text{Co}(\text{NH}_3)_4\text{Br}_2]\text{Cl}$? **[JEE-2005]**

(A) Geometrical and Ionisation
 (B) Optical and Ionisation
 (C) Geometrical and Optical
 (D) Geometrical only

Sol.

Question No. 6 to 8 (3 questions)

[JEE-2006]The coordination number of Ni^{2+} is 4. $\text{NiCl}_2 + \text{KCN (excess)} \rightarrow \text{A (cyanido complex)}$ $\text{NiCl}_2 + \text{Conc. KCl (excess)} \rightarrow \text{B (chlorido complex)}$

6. The IUPAC name of A and B are
 (A) Potassium tetracyanonickelate (II), potassium tetrachloridonickelate (II)
 (B) Tetracyanidopotassiumnickelate (II), tetrachloridopotassiumnickelate (II)
 (C) Tetracyanidornickel (II), tetrachloridonickel (II)
 (D) Potassium tetracyanonickel (II), potassium tetrachloridonickel (II)

Sol.

7. Predict the magnetic nature of A and B

(A) Both are diamagnetic
 (B) A is diamagnetic and B is paramagnetic with one unpaired electron
 (C) A is diamagnetic and B is paramagnetic with two unpaired electrons
 (D) Both are paramagnetic.

Sol.

8. The hybridization of A and B are

(A) dsp^2 , sp^3 (B) sp^3 , sp^3
 (C) dsp^2 , dsp^2 (D) sp^3d^2 , d^2sp^3

Sol.

9. If the bond length of CO bond in carbon monoxides is 1.128 \AA , then what is the value of CO bond length in $\text{Fe}(\text{CO})_5$? **[JEE-2006]**

(A) 1.15 \AA (B) 1.128 \AA
 (C) 1.72 \AA (D) 1.118 \AA

Sol.

10. Among the following metal carbonyls, the C–O bond order is lowest in **[JEE-2007]**

(A) $[\text{Mn}(\text{CO})_6]^+$ (B) $[\text{Fe}(\text{CO})_5]$
 (C) $[\text{Cr}(\text{CO})_6]$ (D) $[\text{V}(\text{CO})_6]^-$

Sol.

11. Match the complexes in Column I with their properties listed in Column II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS. [JEE-2007]

Column I

- (A) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_2$
 (B) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
 (C) $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}$
 (D) $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$

Column - II

- (P) Geometrical isomers
 (Q) Paramagnetic
 (R) Diamagnetic
 (S) Metal ion with +2 oxidation state

Sol.

12. Among the following, the coloured compound is [JEE-2008]

- (A) CuCl (B) $\text{K}_3[\text{Cu}(\text{CN})_4]$
 (C) CuF_2 (D) $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$

Sol.

13. The IUPAC name of $[\text{Ni}(\text{NH}_3)_4][\text{NiCl}_4]$ is [JEE-2008]

- (A) Tetrachloronickel (II)-tetraamminenickel (II)
 (B) Tetraamminenickel (II)-Tetrachloronickel (II)
 (C) Tetraamminenickel (II)-tetrachloronickelate (II)
 (D) Tetrachloronickel (II)-tetraamminenickelate (0)

Sol.

14. Both $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are [JEE-2008]

- (A) sp^3 , sp^3 (B) sp^3 , dsp^2
 (C) dsp^2 , sp^3 (D) dsp^2 , dsp^2

Sol.

15. STATEMENT - 1 $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ is paramagnetic.

and

STATEMENT - 2 The Fe in $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ has three unpaired electrons. [JEE-2008]

(A) STATEMENT - 1 is true, STATEMENT - 2 is true; STATEMENT - 2 is a correct explanation for STATEMENT - 1

(B) STATEMENT - 1 is true, STATEMENT - 2 is true; STATEMENT - 2 is NOT a correct explanation for STATEMENT - 1

(C) STATEMENT - 1 is true, STATEMENT - 2 is false

(D) STATEMENT - 1 is False; STATEMENT - 2 is True

Sol.

16. The spin only magnetic moment value (in Bohr magneton units) of $\text{Cr}(\text{CO})_6$ is [JEE-2009]

- (A) 0 (B) 2.84
 (C) 4.90 (D) 5.92

Sol.

17. The compound(s) that exhibit (s) geometrical isomerism is (are) [JEE-2009]

- (A) $[\text{Pt}(\text{en})\text{Cl}_2]$ (B) $[\text{Pt}(\text{en})_2]\text{Cl}_2$
 (C) $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ (D) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

Sol.

18. The correct structure of ethylenediaminetetraacetic acid (EDTA) is [JEE-2010]

- (A) $\text{HOOC}-\text{CH}_2-\text{N}-\text{CH}=\text{CH}-\text{N}-\text{CH}_2-\text{COOH}$
 (B) $\text{HOOC}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{COOH}$
 (C) $\text{HOOC}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{COOH}$
 (D) $\text{HOOC}-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{COOH}$

Sol.

19. The ionization isomer of $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{NO}_2)]\text{Cl}$ is
 (A) $[\text{Cr}(\text{H}_2\text{O})_4(\text{O}_2\text{N})]\text{Cl}_2$ [JEE-2010]
 (B) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2](\text{NO}_2)$
 (C) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}(\text{ONO})]\text{Cl}$
 (D) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2(\text{NO}_2)] \cdot \text{H}_2\text{O}$

Sol.

20. The complex showing a spin - only magnetic moment of 2.82 B.M. is [JEE-2011]
 (A) $[\text{Ni}(\text{CO})_4]$ (B) $[\text{NiCl}_4]^{2-}$
 (C) $[\text{Ni}(\text{PPh}_3)_4]$ (D) $[\text{Ni}(\text{CN})_4]^{2-}$

Sol.

21. Among the following complexes (K - P), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (K), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (L), $\text{Na}_3[\text{Co}(\text{oxalate})_3]$ (M), $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ (N), $\text{K}_2[\text{Pt}(\text{CN})_4]$ (O) and $[\text{Zn}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (P) the diamagnetic complexes are [JEE-2011]
 (A) K, L, M, N (B) K, M, O, P
 (C) L, M, O, P (D) L, M, N, O

Sol.

22. The colour of light absorbed by an aqueous solution of CuSO_4 is [JEE-2012]
 (A) orange-red (B) blue-green
 (C) yellow (D) violet

Sol.

23. As per IUPAC nomenclature, the name of the complex, $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3$ is [JEE-2012]
 (A) Tetraaquadiaminecobalt (III) chloride
 (B) Tetraaquadiaminocobalt (III) chloride
 (C) Diaminetetraaquacobalt (III) chloride
 (D) Diamminetetraaquacobalt (III) chloride

Sol.

24. $\text{NiCl}_2\{\text{P}(\text{C}_2\text{H}_5)_2(\text{C}_6\text{H}_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic / diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively. [JEE-2012]
 (A) tetrahedral and tetrahedral
 (B) square planar and square planar
 (C) tetrahedral and square planar
 (D) square planar and tetrahedral

Sol.

SUBJECTIVE

1. Why only $[\text{CuCl}_4]^{2-}$ exists but $[\text{CuI}_4]^{2-}$ does not. [JEE-1992]

Sol.

2. Write the IUPAC name of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ [JEE-1994]

Sol.

3. Which type of magnetism is exhibited by $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ ion [JEE-1994]

Sol.

4. Write the IUPAC name of compound $[\text{Cr}(\text{NH}_3)_5(\text{NCS})][\text{ZnCl}_4]$. Is this compound coloured? [JEE-1997]

Sol.

5. Write the IUPAC name of the following complexes
 (i) Pentaamminechloridocobalt (III)
 (ii) Lithium tetrahydridoaluminate (III) [JEE-1997]

Sol.

6. A, B and C are three complexes of chromium (III) with the empirical formula $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H_2SO_4 whereas complexes B and C lose 6.75 % and 13.5 % of their original weight, respectively, on treatment with concentrated H_2SO_4 . Identity A, B and C. [JEE-1999]

Sol.

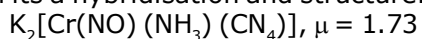
7. Draw the structures of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $\text{Ni}(\text{CO})_4$. Write the hybridisation of atomic orbitals of the transition metal in each case. [JEE-2000]

Sol.

8. Deduce the structures of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ considering the hybridisation. Calculate the magnetic moment (spin only) of the species. [JEE-2002]

Sol.

9. Write the IUPAC name of the given complex along with its a hybridisation and structure.



[JEE-2003]

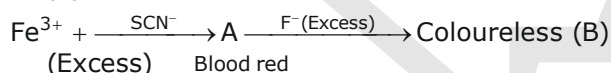
Sol.

10. When dimethyl glyoxime is added to the aqueous solution of nickel (II) chloride in presence of dilute ammonia solution, a rosy red coloured ppt is obtained. [JEE-2004]

- (a) Draw the structure of rosy red substance.
(b) Write the oxidation state of nickel in the substance and hybridisation.
(c) State whether the substance is paramagnetic or diamagnetic.

Sol.

11. In the given reaction sequence, identify (A) and (B)



(Excess) Blood red

- (a) Write the IUPAC name of (A) and (B)
(b) Find out the spin only magnetic moment of B. [JEE-2005]

Sol.

12. The number of water molecule(s) directly bonded to the metal centre in $CuSO_4 \cdot 5H_2O$ is [JEE-2009]

Sol.

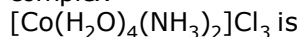
13. The volume (in mL) of 0.1 M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to [JEE-2011]

Sol.

14. The colour of light absorbed by an aqueous solution of $CuSO_4$ is [JEE-2012]
(A) orange-red (B) blue-green
(C) yellow (D) violet

Sol.

15. As per IUPAC nomenclature, the name of the complex [JEE-2012]



- (A) Tetraaquadiaminocobalt (III) chloride
(B) Tetraaquadiamminocobalt (III) chloride
(C) Diaminetetraaquacobalt (III) chloride
(D) Diamminetetraaquacobalt (III) chloride

Sol.

16. $NiCl_2 \cdot \{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behaviour (paramagnetic / diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively. [JEE-2012]

- (A) tetrahedral and tetrahedral
(B) square planar and square planar
(C) tetrahedral and square planar
(D) square planar and tetrahedral

Sol.

17. Consider the following complex ion P, Q and R
 $P = [FeF_6]^{3-}$, $Q = [V(H_2O)_6]^{2+}$ and
 $R = [Fe(H_2O)_6]^{2+}$ [JEE-2013]

The correct order of the complex ions, according to their spin-only magnetic moment value (in B.M.) is

- (A) $R < Q < P$ (B) $Q < R < P$
(C) $R < P < Q$ (D) $Q < P < R$

Sol.

18. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) [JEE-2013]

- (A) $[Cr(NH_3)_5Cl_2]^+$ and $[Cr(NH_3)_4Cl_2]Cl$
(B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$
(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$
(D) $[Pt(NH_3)_3(NO_3)]Cl$ and $[Pt(NH_3)_3Cl]Br$

Sol.

19. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N-Co-O bond angles in $[Co(EDTA)]^{1-}$ complex ion is [JEE-2013]

Sol.

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. B | 2. D | 3. D | 4. C | 5. B | 6. A | 7. B |
| 8. C | 9. B | 10. B | 11. A | 12. D | 13. D | 14. C |
| 15. C | 16. C | 17. C | 18. D | 19. B | 20. A | 21. D |
| 22. D | 23. A | 24. B | 25. C | 26. C | 27. D | 28. B |
| 29. B | 30. D | 31. B | 32. B | 33. A | 34. A | 35. C |
| 36. D | 37. B | 38. B | 39. D | 40. B | 41. B | 42. C |
| 43. D | 44. C | 45. B | 46. C | 47. D | 48. B | 49. D |
| 50. B | 51. A | 52. C | 53. C | 54. D | 55. C | 56. B |
| 57. B | 58. C | 59. D | 60. C | 61. D | 62. B | 63. D |
| 64. C | 65. C | 66. C | 67. D | 68. A | 69. A | 70. B |

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

One or more than correct :

- | | | | | | | |
|----------|----------|---------|--------|--------|---------|---------|
| 1. AD | 2. C | 3. ABD | 4. AD | 5. ACD | 6. ACD | 7. A |
| 8. BCD | 9. AC | 10. BD | 11. BD | 12. BD | 13. ABD | 14. ABD |
| 15. ABCD | 16. ABCD | 17. ABD | 18. BD | 19. AB | 20. BCD | 21. AC |
| 22. ABCD | 23. BCD | | | | | |

Comprehension Type :

24. D 25. B 26. B 27. A 28. C 29. B 30. B
31. A 32. A 33. B 34. B

Match the column :

35. A - S ; B - P; C - Q 36. A - R, S ; B - P Q ; C - P; D - P, Q
37. A - P, S ; B - P, S ; C - Q; D - Q, R 38. A - P ; B - P ; C - Q; D - R
39. A - P, R, S ; B - T ; C - Q, R, T ; D - P, R, S 40. A - R ; B - R ; C - P; D - Q
41. A - Q, S, T ; B - P, R ; C - P, R; D - P, R 42. A - Q ; B - P, Q ; C - R, S ; D - R, S
43. A - P, Q, R, S ; B - Q, R ; C - P, Q ; D - P, Q, R, S 44. A - P, Q ; B - P, R ; C - R, S

Answer Ex-III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. B 2. C 3. C 4. B 5. C 6. C 7. B
8. C 9. B 10. B 11. C 12. C 13. C 14. D
15. D 16. D 17. C 18. C 19. B 20. C 21. C
22. B 23. C 24. B 25. D 26. D 27. D 28. D
29. A 30. A 31. D 32. D 33. B 34. C 35. D
36. A 37. C 38. A 39. A 40. C 41. B 42. A

Answer Ex-IV**PREVIOUS YEARS****LEVEL - I****JEE MAIN**

1. B 2. C 3. D 4. A 5. C 6. B 7. A
8. C 9. D 10. C 11. C 12. A 13. B 14. D
15. D 16. A 17. C 18. D 19. D 20. A 21. C
22. A

LEVEL – II

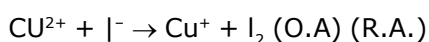
JEE ADVANCED

Objective :

1. B 2. D 3. B 4. B 5. A 6. A 7. C
8. A 9. A 10. D 11. A – P, Q, S ; B – P, R, S ; C – Q, S ; D – Q, S
12. C 13. C 14. B 15. A 16. A 17. CD
18. C 19. B 20. B 21. C 22. A 23. D 24. C

Subjective :

1. Reducing power of
- $I^- > Cl^-$



2. Hexaamminecobalt (III) chloride

3. Paramagnetism
- $m = \sqrt{35}$
- B.M

4. Pentaamminethiocyanato-N-chromium (III) tetrachloridozincate (II), Yes

- 5.
- $[Co(NH_3)_5Cl]^{2+}$
- ,
- $Li[AlH_4]$

6. A =
- $[Cr(H_2O)]Cl_3$
- , B =
- $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
- , C =
- $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

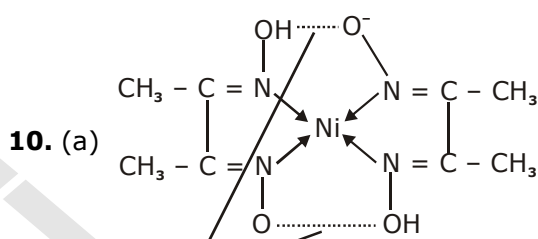
- 7.
- $[Co(NH_3)_6]^{3+}$
- d^2sp^3
-
- Octahedral

- $[Ni(CN)_4]^{2-}$
- dsp^2
-
- Square planar

- $[Ni(CO)_4]$
- sp^3
-
- Tetrahedral

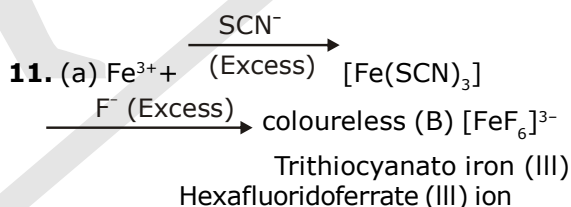
8. Tetrahedral,
- $\sqrt{8}$
- B.M. Square planar,
- $\mu = 0$
- B.M.

- 9.
- $K_2[Cr(NO)(NH_3)(CN)_4]$
- ,
- $m_{eff} = 1.73$
- BM. Chromium is 1 + oxidation state and hybridization is
- d^2sp^3
- and IUPAC name is Potassium aminetetracyanonitrosomchromate(I) and Octahedral shape.

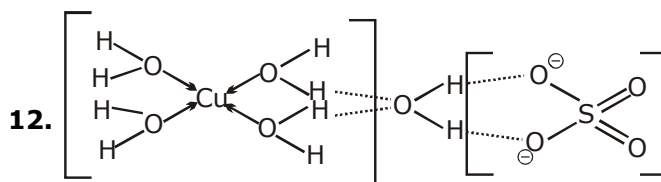


- (b)
- dsp^2
- hybridization square planar structure and oxidation state of Ni = 2+

- (c) Diamagnetic



- (b) The magnetic moment value of B is 5.93 B.M.



13. 0006 14. A 15. D 16. C
17. B 18. B,D 19. 0006

METALLURGY

Minerals : Naturally occurring chemical substance in which metal exists either in its free state or in combined state is called mineral.

Ore : Mineral from which metal can be conventionally and economically extracted is called ore & impurities associated with it is called gangue or matrix

TYPES OF ORES :

- **Sulphide Ores** : Galena : PbS , Cinnabar : HgS ,
Zinc blende : ZnS , Chalcopyrite : CuFeS_2 ,
Copper glance : Cu_2S Fool's Gold : FeS_2
- **Oxide Ores** :
Bauxite : $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ Haematite : Fe_2O_3
Limonite : $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ Tin stone or Cassiterite : SnO_2
- **Carbonate Ores** : Siderite : FeCO_3 Calamine ZnCO_3
Malacite : $\text{Cu}(\text{OH})_2\text{CuCO}_3$ Dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot 2\text{H}_2\text{O}$
lime stone : CaCO_3
- **Sulphate Ores** : Gypsum : $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Anhydrite PbSO_4
Glauber's salt : $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ Mohr's salt : $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
- **Halide Ores** : Rock salt : NaCl Cryolite : Na_3AlF_6
Fluorspar : CaF_2 Carnallite : $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
- **Nitrate Ores** : Chile Saltpetre : NaNO_3 Indian Salt petre : KNO_3
- **Native Ores** : Those metals which are chemically less reactive. They occur in the earth crust in form of free state (lumps)
e.g : Cu, Ag, Au, Hg, Pd, Pt, Bi

General principles and processes involved in the extraction of metal from its ore :

The extraction of metal from its ore is completed in five steps :

Step I : Pulverization : The crushing of ore to powdered state is called pulverisation.

Step II : concentration or Dressing or Beneficiation of ore

Step III : Conversion of Concentrated ore into oxide form

step IV : Reduction of oxide to the metal

Step V : Purification or refining of crude metal :

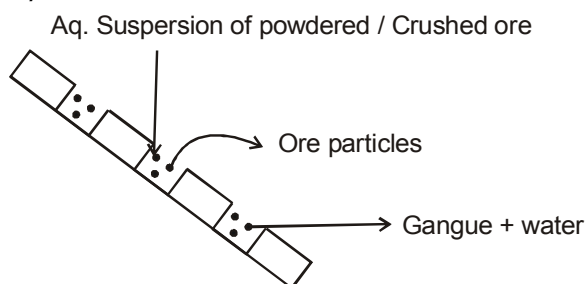
Step I : Pulverization : The crushing of ore to powdered state is called pulverisation

This process in stamp mill or ball mill

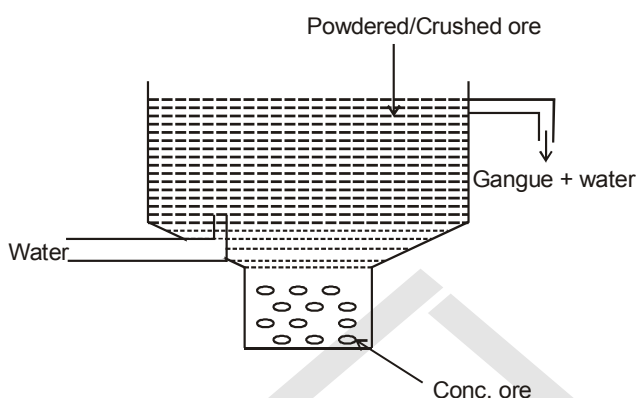
Step II : Concentration or Dressing or beneficiation of Ore

- (a) **By Gravity separation** : Ore particles are heavier than the gangue particles. This is used for the separation of most of the gangue particles :

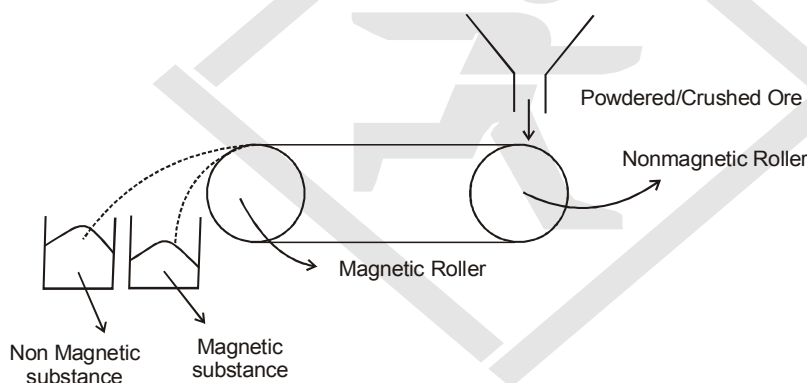
⇒ By Wilfley Table Method



⇒ By Hydraulic Classifier



(b) By Magnetic separator :



Cassiterite or Tinstone contains impurities of wulframite or wulframates of Fe & Mn.

⇒ Tin stone : $\text{SnO}_2 \rightarrow$ Diamagnetic

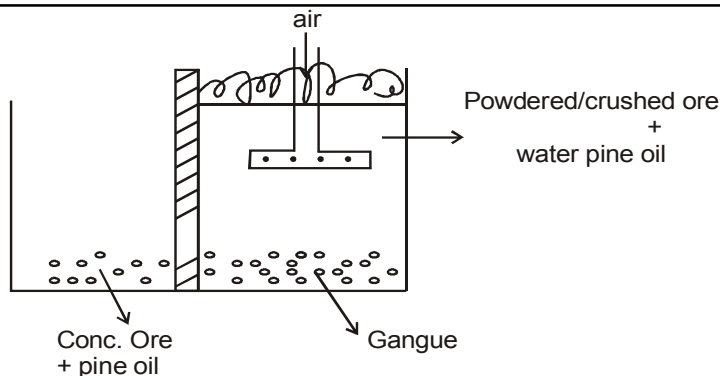
⇒ Wulframites or wulframates of

Fe & Mn : $\text{FeWO}_4, \text{MnWO}_4 \Rightarrow$ Paramagnetic.

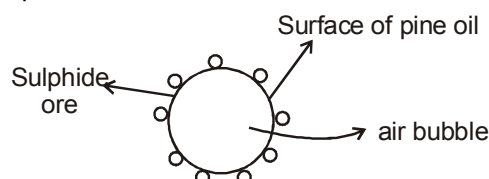
Ulframates of Fe & Mn from Tin stone by magnetic separator.

(c) By Froth Floatation Process : This method is used for the concentration of sulphide ores.

- It is based on the concept that the sulphide ores are preferentially wetted by pine oil, camphor oil while gangue particles are preferentially by water.
- This is based on the physical phenomenon of adsorption.

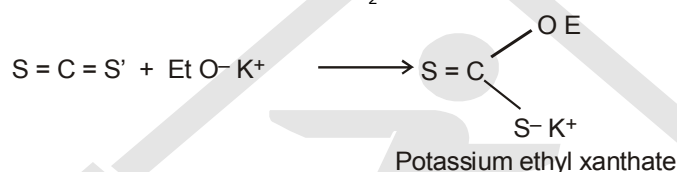
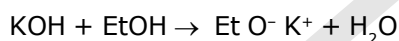


Frother : Pine oil, Camphor oil



Froth Stabilizers : They reduce surface tension of water e.g. cresols, amines.

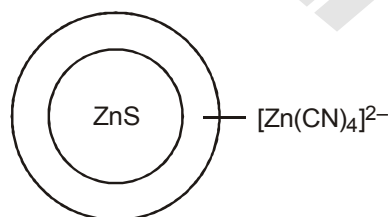
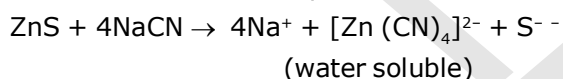
Collector : Sodium or Potassium xanthates. It combines with sulphide ore & makes them water repellent so that its affinity towards pine oil increases (Adsorption tendency increases)



Depressant : KCN or NaCN

ZnS is found to be an impurity with the lead sulphide. Therefore to separate out PbS from ZnS depressant KCN or NaCN added.

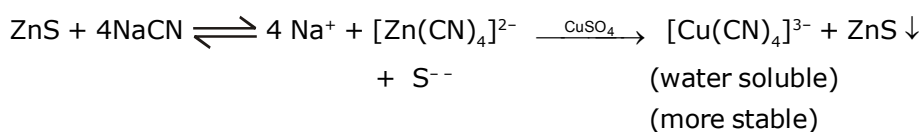
$\text{PbS} + \text{NaCN} \rightarrow$ No complex formation due to very low K_{sp} of PbS.



Thus, ZnS becomes water soluble & it remains with gangue while PbS comes out with the froth.

Activator : CuSO_4

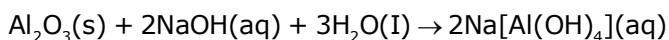
From galena (PbS.ZnS) ZnS is removed



& ZnS is taken out by froth floatation second time.

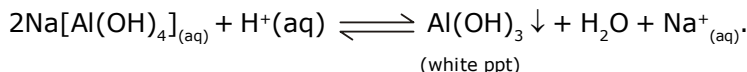
(ii) Chemical Method of Concentration :

Leaching : It involves dissolution of metallic ore in a suitable reagent in which metallic ore is soluble and impurities are insoluble.

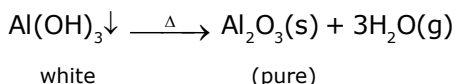
Leaching of alumina from bauxite :

Having F_2O_3 as important leachant.

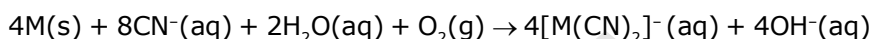
The aluminate in solution is acidified by adding acid and hydrated Al_2O_3 is precipitated.



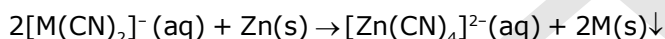
Hydrated alumina is filtered, dried and heated to give back pure Al_2O_3 :

**Other examples :**

In the metallurgy of silver and gold, the respective metal/ore is leached with very dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained by displacement reaction.



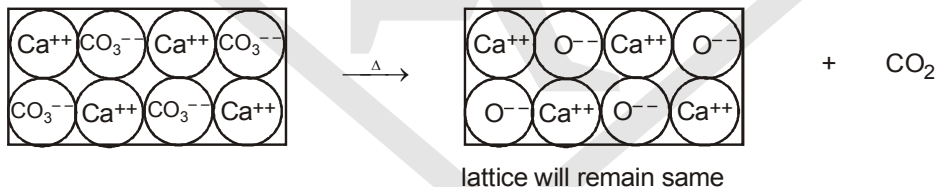
(M = Ag Or Au)

**Step III : Conversion of Concentrated ore into oxide form :**

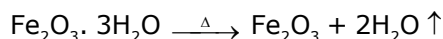
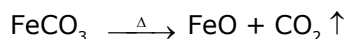
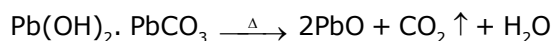
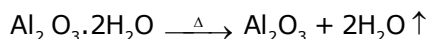
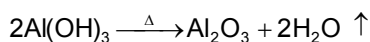
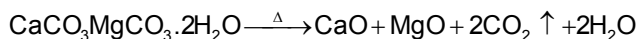
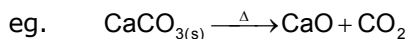
It is done either by calcination or by roasting.

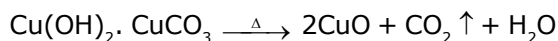
(i) Calcination :

- Calcination is carried out for carbonate, hydrated metal oxide & metal hydroxide ores.
- It is carried out in the absence of air i.e., heating in absence of air.

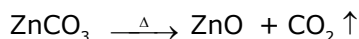


- Due to calcination ore becomes porous.
- Volatile organic impurities get evaporated



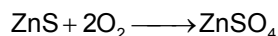
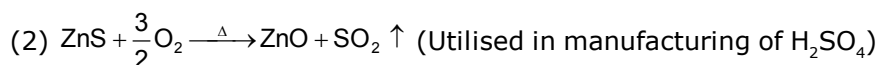
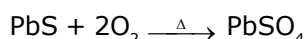
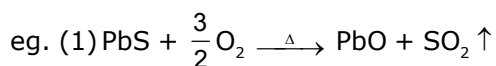


Black powder



(ii) Roasting : In the presence of air the sulphide are heated in free supply of air below m.p. Impurities of sulphur, phosphorus, arsenic & antimony are converted into their corresponding volatile oxide & thus get removed.

Moisture & Water of crystallisation are also removed.



step IV : Reduction of oxide to the metal :

(b) Reduction of Metal oxide / conc. ore into free metal .

This can be carried out

- | | |
|-----------------------------------|---|
| (i) chemical reduction | (ii) By self reduction or auto reduction or Air Reduction |
| (iii) Metal - displacement method | (iv) By electrolytic Reduction (v) By amalgamation. |

(i) & (ii) method are collectively known as Pyrometallurgy

e.g. Sn, Pb, Fe, Hg, Cu, B, Zn, (Based on Ellingham diagram)

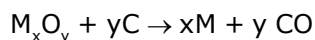
(iii) step is called hydrometallurgy — Cu, Ag, Au are extracted

(iv) step is called Electrometallurgy, Alkali, Alkaline earth metals & Al & base electrolysis

(v) is used for Ag & Au

(I) CHEMICAL REDUCTION :

1. Smelting i.e., carbon Reduction - Reduction of metal oxide by coke, coal & CO Reduction of the metal oxide usually involves heating it with some other Substance acting as a reducing agent, e.g., C or CO or even another metal. The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

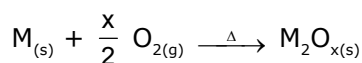


Some metal oxides get reduced easily while others are very difficult to be reduced. To understand the variation in the temperature requirement for thermal reductions and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are done, which is explained by ellingham diagram.

$$\therefore \Delta G = \Delta H - T\Delta S$$

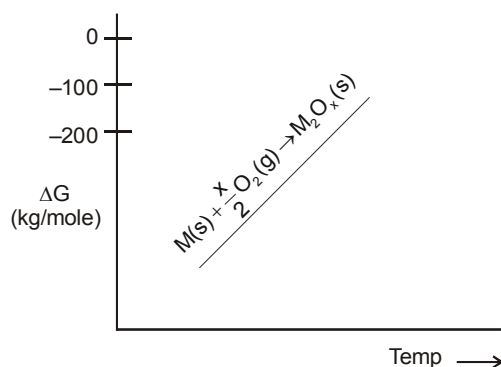
If ΔH is greater than zero then reduction will be feasible on increasing temprature i.e., $|T\Delta S| > |\Delta H|$

Ellingham diagram -



$$\Delta G = \Delta H - T\Delta S$$

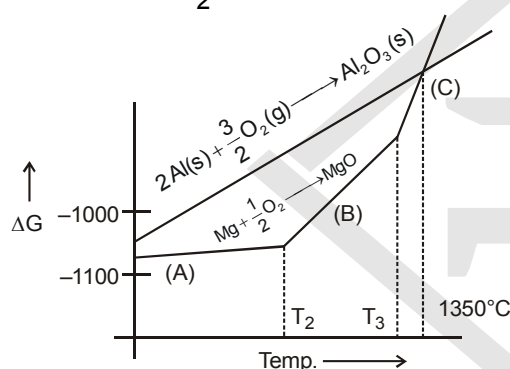
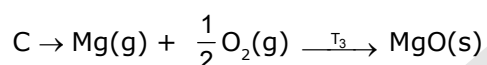
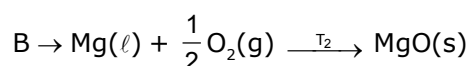
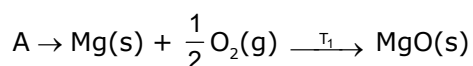
∴ For forward rxn $\Delta S < 0$



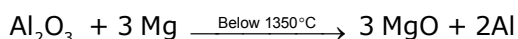
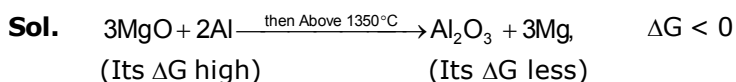
(Ellingham diagram for formation of M_2O_x)

Ellingham diagram is a plot of formation of an element oxide between ΔG & ΔT

Ex. Which of the following statements are true :

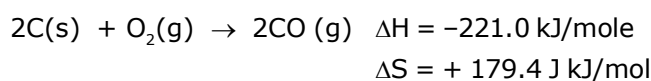


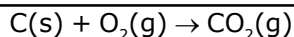
- I : Below 1350° Mg can reduce Al_2O_3
- II : Above 1350° C Mg Will reduce Al_2O_3
- III : Below 1350° Al can reduce MgO
- IV : Above 1350° Al can reduce MgO
- V : At 1350° C there is no change in free energy i.e., $\Delta G = 0$



At 1350° C both reactions have same G ∴ $\Delta G = 0$

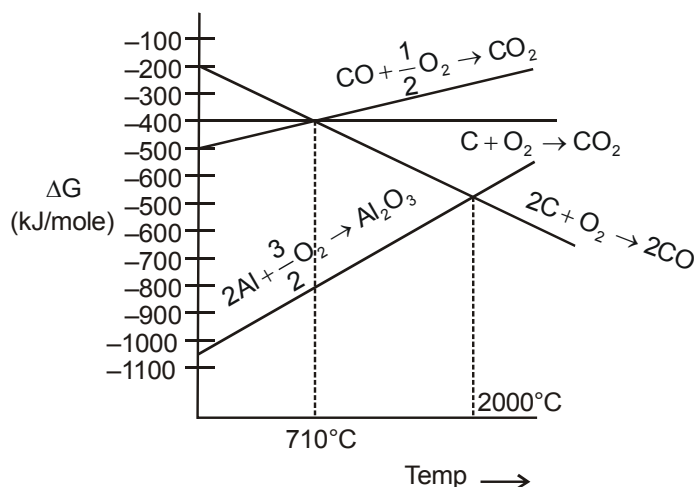
To carry out smelting below 800°C, CO is used as reducing agent while above 800°C, smelting is carried out by coke.



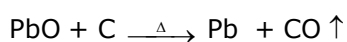
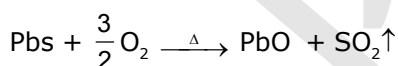
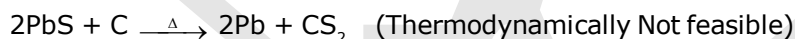


$$\Delta H = -393.5 \text{ kJ/mol}$$

$$\Delta S = 2.89 \text{ JK}^{-1} \text{ mole}^{-1}$$



- Aluminium can be extracted from Alumina by carbon reduction but the method is highly uneconomical because -
 - As the smelting occurs above 2000°C hence a part of the aluminium will go into vapour phase (M.P. = 2520°C)
 - At this high temperature the liberated Al will combine with the carbon & aluminium carbide will be formed.
 - ΔH_{for} of alumina is high - ve value
 \therefore It is thermodynamically more stable & reduction is more difficult
- To extract metal from sulphide ore is carried out by firstly roasting it into metal oxide & followed by its smelting. Metal sulphide or sulphide ore is not directly smelted to metal.



} Thermodynamically feasible

$$\Delta G_f \text{ of PbS} = -21.9 \text{ kcal/mol}$$

$$\Delta G_f \text{ of CS}_2 = +17.15 \text{ kcal/mol}$$

$$\Delta G_f \text{ of PbO} = -45.1 \text{ kcal/mol}$$

$$\Delta G_f \text{ of SO}_2 = -71.7 \text{ kcal/mol}$$

$$\Delta G_f \text{ of CO} = -32.8 \text{ kcal/mol}$$

Flux : Additional substances which are used during metal extraction to remove acidic or basic impurity are called flux depending upon nature of impurity flux are of two types.

(i) Basic Flux : It is used to remove acidic impurity eg : CaO, MgO, CaCO₃, MgCO₃, FeCO₃ etc.

(ii) Acidic Flux : It is used to remove basic impurity eg : SiO₂, B₂O₃, P₂O₅, Na₂B₄O₇. (Borax)

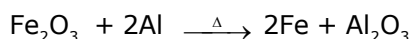
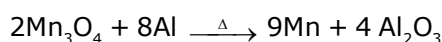
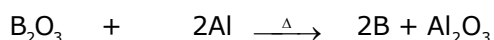
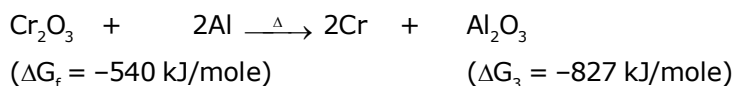
Smelting : Phenomenon of slag formation by combining flux with impurity is called smelting.

Flux + Impurity \longrightarrow Slag (Smelting)

(Basic or acidic)

Properties of slag :

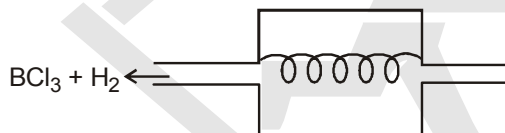
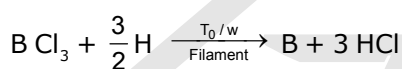
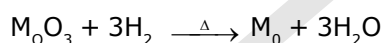
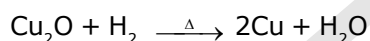
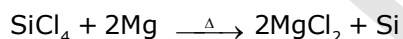
- (i) Slag has low melting point than metal.
- (ii) Slag is lighter than metal therefore it floats over the molten metal and prevents further oxidation of molten metal by air.
- (iii) Slag immiscible with molten metal therefore it can be easily separated from molten metal.

(b) Gold Schmidt Thermite Reduction :**Thermite : Al powder**

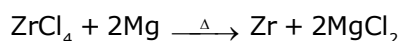
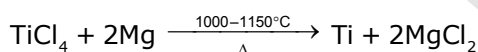
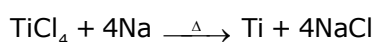
This method is used for reduction of those metal oxides which are highly stable if they are reduced by coke it will occur at very high temperature & at this high temperature the liberated metal will combine with the coke & carbide will be formed hence Al powder i.e., thermite is used

(c) Reduction by Hydrogen :

Because of inflammable nature of hydrogen its use as a reducing agent is very restricted.

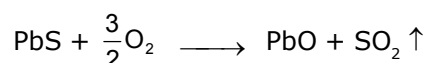
**Reduction by other metals :**

Kroll process used for extraction of Ti & Zr

**I.M.I Process (Imperial Metal Industries)****(ii) By Self reduction or Auto reduction or Air Reduction :**

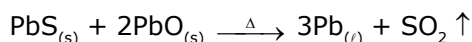
This method is used for extraction of copper, lead, mercury i.e., it is used for the extraction of metal from their sulphide ores.

In this method the sulphide ore is roasted in free supply of air to its metal oxide & then air supply is cut off followed by heating by increasing temperature & metal is extracted by self reduction.



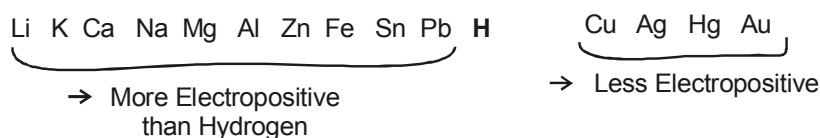


Now air supply is cut off followed by heating



Self reduction is responsible for acid rain than roasting because SO_2 dissolves in air, (3927cc CO_2 in 1000cc of H_2O)

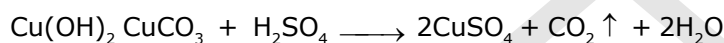
(iii) By Metal Displacement Method or By Hydrometallurgy :



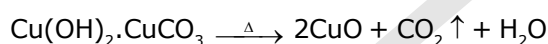
In this method the concentrated ore is treated/ leached with specific chemical reagent that converts the ore into water soluble salt. Now, on adding more electropositive metal into the aqueous salt solution the metal (less electro positive) is displaced

e.g.

Extraction of Copper from Malacite :

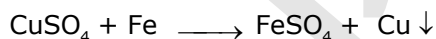


or



$\text{H}_2\text{SO}_4 \Rightarrow$ leaching agent, it leached out Cu as CuSO_4

Now, on adding more electropositive metal :



(Reducing agent)

$$\therefore E^\circ_{\text{Cu}^{++}/\text{Cu}} = +0.34$$

$$E^\circ_{\text{Fe}^{++}/\text{Fe}} = -0.40$$

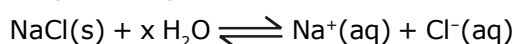
$$\therefore E^\circ_{\text{Cell}} = 0.74 \quad \Rightarrow \quad \Delta G < 0$$

- Iron is found to be an impurity in the copper ores hence if Zn is added to extract copper, iron will also be displaced along with copper & that is why iron is used.
- Both metals which extracted & by which we extracted are water insoluble

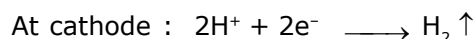
(iv) Electro Metallurgy : The metal is extracted by passing electricity into its fused salt or in aqueous solution.

Extraction of sodium :

\Rightarrow By electrolysis of Aq. NaCl solution :



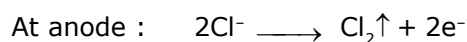
- On passing electricity



$$\therefore E^\circ_{\text{H}^+ / 1/2\text{H}_2=0}; \Delta G = -nFE^\circ$$

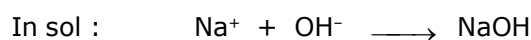
$$E^\circ_{\text{Na}^+ / \text{Na}} = -2.7 \text{ V}; \Delta G = -nFE^\circ$$

$\therefore \text{Na}^+$ does not discharge at cathode

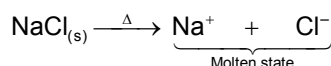


$$E^\circ_{1/2\text{Cl}_2 / \text{Cl}^-} = -1.36 \text{ Volt}$$

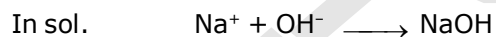
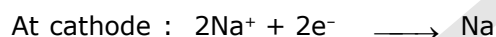
$$E^\circ_{1/2\text{O}_2 / \text{OH}^-} = -0.44 \text{ V}$$



\Rightarrow By electrolysis of fused NaCl :



On Passing electricity



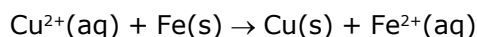
Electrochemical Principles of Metallurgy :

We have seen how principles of thermodynamics are applied to pyrometallurgy. Similar principles are effective in the reductions of metal ions in solution or molten state. Here they are reduced by electrolysis or by adding some reducing element.

In the reduction of molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which could be understood through the equation,

$$\Delta G^\circ = -nE^\circ F \dots\dots\dots (16)$$

Here n is the number of electrons and E° is the electrode potential of the redox couple formed in the system. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E° values corresponds to a positive E° and consequently negative ΔG° in equation (16), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g.,



In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

Step V: Purification or refining of crude metal :

(A) By physical Methods :

- (a) liquation
- (b) Distillation
- (c) Zone refining

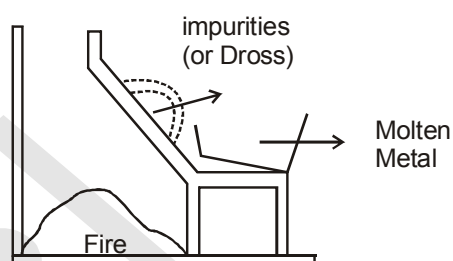
(B) By Chemical Methods

- (a) Oxidation
- (b) Poling
- (c) Vapour Phase Refining

(C) By Electrolytic Refining

(A) By Physical Method :**(a) Liquation Method :**

	Metal	M.P.
Impurities	Sn	232°C
	Fe	1535°C
	Mn	1244°C
	W	3380°C

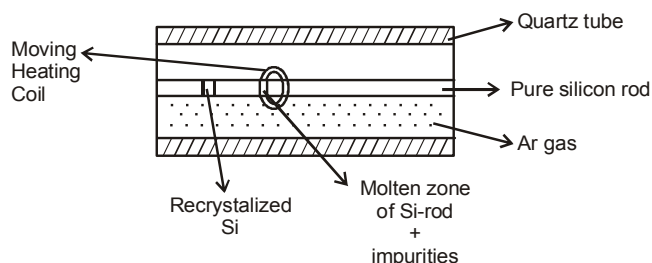
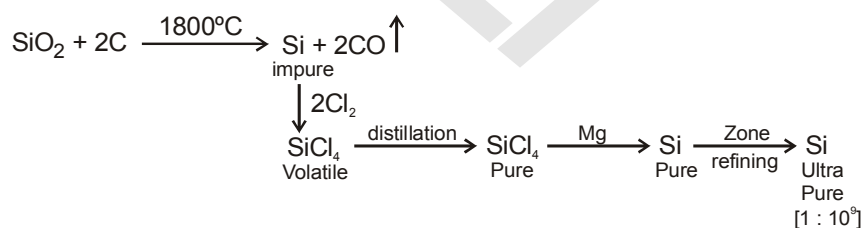


This method is used for refining of those metal which have very low m.p. in comparison to impurity present in them.

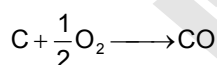
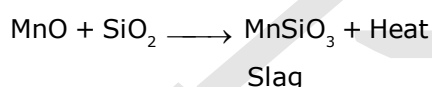
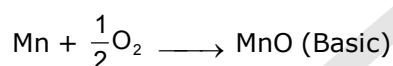
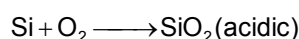
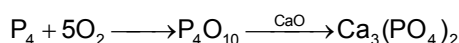
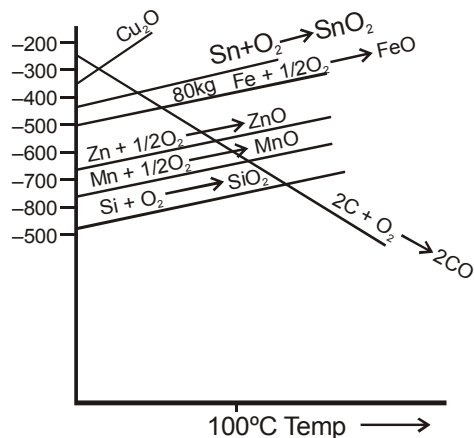
e.g. → Sn, Pb, Hg, Bi, Zn

(b) Distillation Method : It is used for refining of those metals which are volatile & hence it is used for refining of Zn, Cd, Hg (i.e., is of filled d orbital metal)

(c) Zone Refining : (Si, Ge, Pb, B, Ga, In)

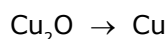


Concept : Impurities are more soluble in the melt than in the solid state. (Fractional crystallization)

(B) By Chemical Methods :**(a) Oxidation : (Fe, Sn, Pb)**eg. **Pig iron** : M.P. 1080**Impurities** : C, P, Mn, Si

This method is used for the refining of metals in which impurities are more oxidisable than metal itself. When impurities oxidise they are converted into either volatile oxides or non volatile oxides. Non-volatile oxides are removed either by slag formation or by removing their skim. Oxidation is known by various names : basessmerization (Fe), Cupellation (Ag), Softening (Pb) or Puddling (for iron), tossing (for iron).

- (b) Polling** : When along with impurities the metal to be refine is also oxidised part then this method is used. In this method the molten impure metal is steared with green wood log, The hydrocarbons released from the log reduce metal oxide into metal while impurity oxides are not reduced. This method is used for refining of Cu & Tin. In both metals during poling iron get oxidised into FeO which in turn is oxidised into Fe₂O₃ while in case of Sn, SnO₂ is reduced to tin (Sn) & in case of Cu copper (I) oxide i.e., cuprous oxide is reduced to Cu,



- (c) Vapour Phase Refining** : Impure metal is allowed to react with a suitable reagent such that a volatile unstable compound is formed & then the compound is decomposed to pure free metal when it is subjected to heat.

- Mond's Process : used for refining of Ni



(C) By Electrolytic Refining :**Anode :** Impure metal**cathode :** Pure metal**Electrolyte :** Aq. salt sol. of metal/fused metal salt + Acid**Anode Mud :** Metals which are less electropositive than the metal to be refined.

In electrolyte : More electropositive metals are found.

eg. in Cu : Ag, Au, Fe, Zn

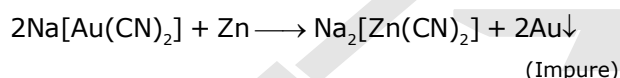
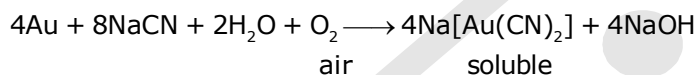

 In electrolyte

1. Gold :**Occurrence :**

Found mostly in free state in quartz veins called auriferous quartz.

Extraction of gold from native ore :**(A) Crushing and concentration :**

The gold ore is crushed, powdered finely and concentrated by washing with water.

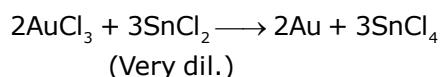
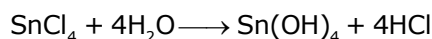
(B) (Treatment with 0.25–1% sodium cyanide or potassium cyanide solution) Extraction of Au, from Native ore by **Mac-Arthur forrest cyanide process**.

Impure Au is purified by Electrolytic refining method or by amalgamation.

(C) Electrolytic refining method :

Anode : Impure Au

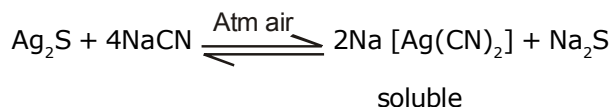
Cathode : Pure Au

Electrolyte : 4% AuCl_3 solution acidified with 10% HCl**Purple of Cassius :** It is of colloidal gold solution :The gold thus precipitated is absorbed by $\text{Sn}(\text{OH})_4$ formed by hydrolysis of SnCl_4 

This form of gold is purple in colour named after its discoverer, Cassius.

2. Silver :**Ores :** (i) Silver glance or argentite Ag_2S (main ore)(ii) Ruby silver or pyrargyrite $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ (iii) Horn silver or chlorargyrite AgCl .**Extraction of silver from silver glance :****(A) Crushing and concentration :** The ore is crushed, powdered and concentrated by froth floatation process.

(B) Extraction of Ag by Mac-Arthur forrest cyanide process : (Treatment with 0.4-0.7% sodium cyanide solution)



The role of air is to oxidise Na_2S so that reaction proceed in the forward direction.

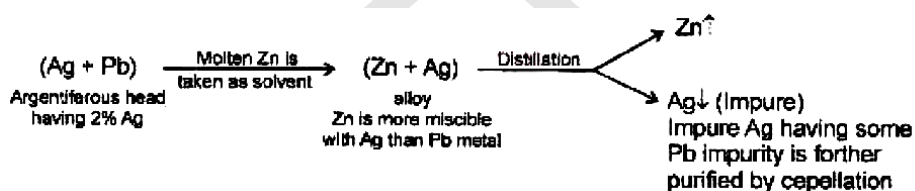
Impure Ag is purified by Electolytic refining method or by amalgamation.

(C) Electrolytic refining :	Anode	:	Impure Ag
	Cathode	:	Pure Ag
	Electrolyte	:	$\text{AgNO}_3(\text{aq}) + \text{HNO}_3$.

Silver from (commercial lead) argentiferous lead by Parke's process :

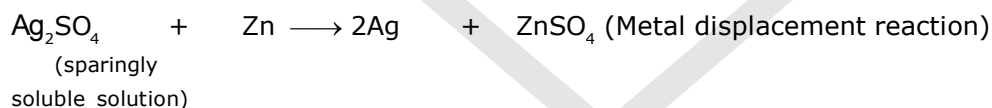
Desilverisation of Lead :

Lead extracted from galena (PbS) contains impurities of Cu, Ag, Bi, As, Fe Zn, Sn, etc. and is called commercial lead or argentiferous lead. This contains Ag upto 2% which is extrated by parkes process. Commerical lead is mixed with a large quantity of Zn and the mixture is melted, where Zn-Ag alloy is formed and Pb remains in the molten state. The alloy is strongly heated where Zn is distilled of leaving Ag. This silver contains some Pb impurity which is removed by cupellation process. Impure Ag is melted in a cupel (a boat shaped dish made of bone ash) by passing Hot blast of air. Pb is oxidised to PbO (litherge) which is either absorbed by cupel or carried away by blast of air leaving pure Ag.



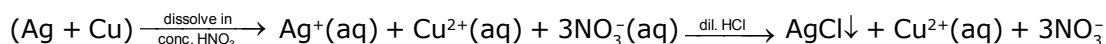
Separation of silver from gold (Parting with conc. H_2SO_4)

Alloy ($\text{Au} < 20\%$) is boiled with conc. H_2SO_4 where Ag is dissolved as Ag_2SO_4 and Au remains as spongy mass.



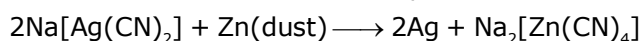
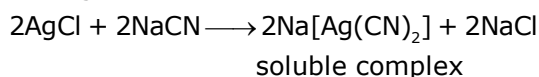
If alloy contains $\text{Au} > 20\%$, then some Ag is added to it so as to reduce the % Au below 20.

Silver from silver coin or silver ornaments :

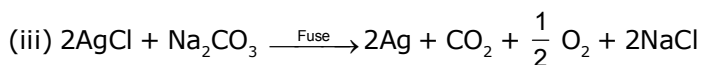
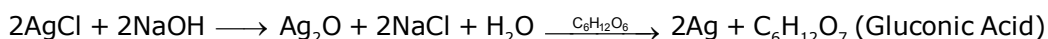


Recovery of Ag from AgCl :

(i) By treating with KCN solution :



(ii) Boiling with caustic soda and glucose.



3. Copper :

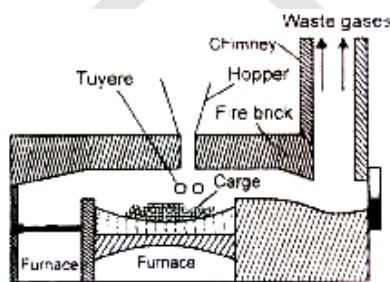
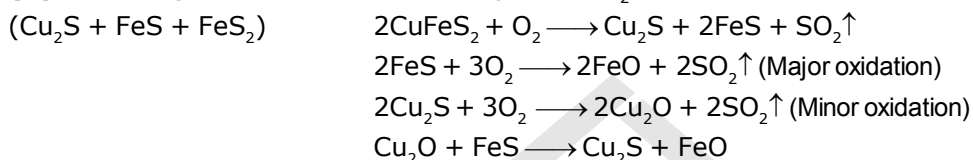
Ores :

Copper pyrites or Chalcopyrites CuFeS_2 (main ore) ; Cuprite or ruby copper Cu_2O ; Malachite $\text{CuCO}_3\text{Cu}(\text{OH})_2$ (green) ; Azurite $2\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ (Blue) ; Copper glance Cu_2S , bornite (peacock ore) Cu_5FeS_4 .

Extraction of copper from copper pyrites :

(A) Crushing and concentration : Ore is first crushed and then powdered finely and powdered ore is concentrated by froth floatation process.

(B) Roasting : Concentrated ore along with SiO_2 is heated in excess of air in a reverberatory furnace.



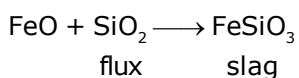
Reverberatory Furnace



Volatile impurities are removed in this step.

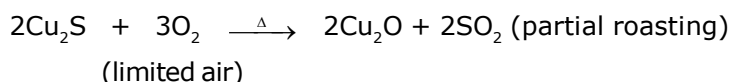
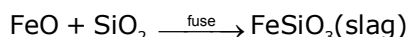
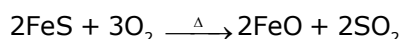
(C) Slag formation :

Roasted ore mixed with sand and strongly heated in furnace.



Upper layer containing slag is removed and lower layer contains mostly Cu_2S (98%) with little amount of FeS (2%) is called **matte**.

(D) Bessemerisation : (Self – reduction)



(R.A.) (impure)

Waste gases

Acidic lining of SiO_2

Tuyeres

Hot air

Molten matte + Sand

Corporate Head Office : Motion Education Pvt. Ltd., 394 - Rajeev Gandhi Nagar, Kota-5 (Raj.)

5. Tin :

Ores : (i) Cassiterite or Tin stone SnO_2 (Main ore) (It contains impurities of pyrites of Cu and Fe and magnetic impurity of wolframite which is a mixture of $\text{FeWO}_4 + \text{MnWO}_4$).

This mineral is also called black tin to distinguish it from the metal Sn which is also called white tin.

Extraction of Sn from cassiterite :**(i) Crushing and concentration :**

The ore is crushed and washed with a stream of running water to remove lighter silicious impurities followed by magnetic separation method to remove the magnetic impurity of Wolframite.

(ii) Roasting :

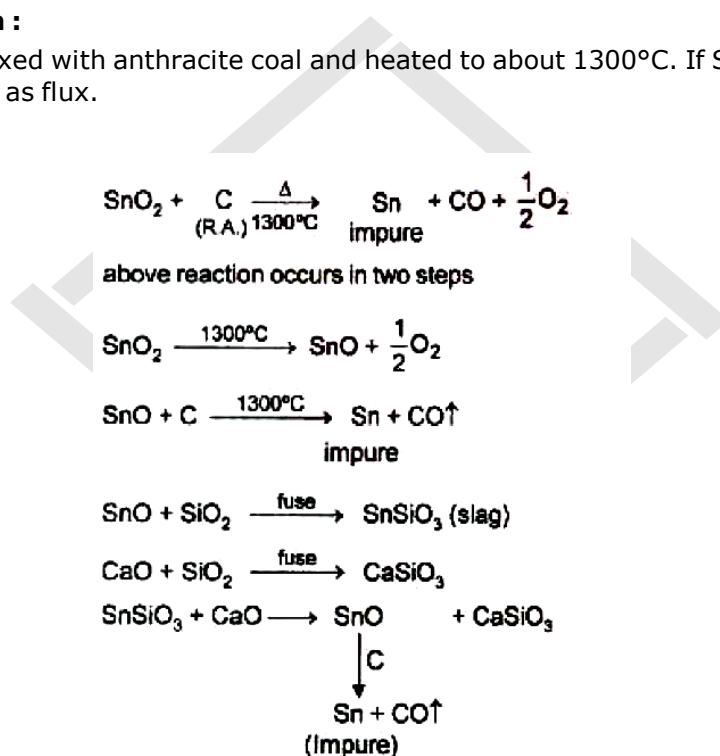
Concentrated ore is heated in presence of air, and volatile impurities (S as SO_2 , As as As_2O_3 and Sb as Sb_2O_3) are removed. The impurities of pyrites of Cu and Fe are converted into their respective oxides and sulphates.

(iii) Washing :

Sulphates of copper and iron are dissolved in water. The ore thus obtained contains 60–70% SnO_2 and is called as black tin.

Carbon reduction :

The black tin is mixed with anthracite coal and heated to about 1300°C . If SiO_2 is present as impurity then CaO is added as flux.

**Refining :****(i) Liquation and poling :**

Impure Sn is melted on the sloping hearth where Sn (m.pt. 232°C) is first melt and flows out leaving behind the less fusible impurities of Cu, Fe, W etc. The liquid Sn is then stirred with poles of green wood to reduce SnO_2 (Impurity) to Sn.

(ii) Electrolytic refining :

Anode : Impure Sn

Cathode : Pure Sn

Electrolyte : $\text{SnSO}_4 + \text{H}_2\text{SO}_4$

6. Iron :

Ores : Haematite Fe_2O_3 (Main ORE) ; Limonite $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; Magnetite Fe_3O_4 ; Siderite FeCO_3 ; Iron pyrites FeS_2

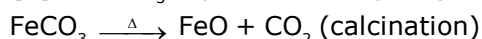
Extraction of Iron from ore haematite :

Crushing and concentration : The oxide ore is first crushed in jaw crushers and then is broken in small pieces. Haematite (non-magnetic) is washed with running water to remove earthy and siliceous impurities by levigation.

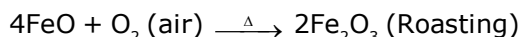
Calcination following by roasting :

The concentrated ore is roasted with excess air in a reverberatory furnace. During roasting step, the following changes occur :

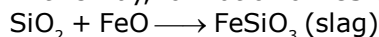
(a) If FeCO_3 is present as impurity, it gets decomposed into FeO which is oxidised by air to Fe_2O_3 .



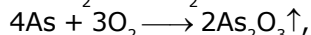
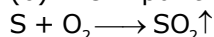
siderite



In this way, formation of FeSiO_3 slag is prevented during melting, and following reaction does not occur.



(b) The impurities of S, As are also removed as their volatile oxides



The entire mass becomes porous and hence the reduction of Fe_2O_3 to spongy iron becomes easy at later stage.

Reduction in blast furnace.

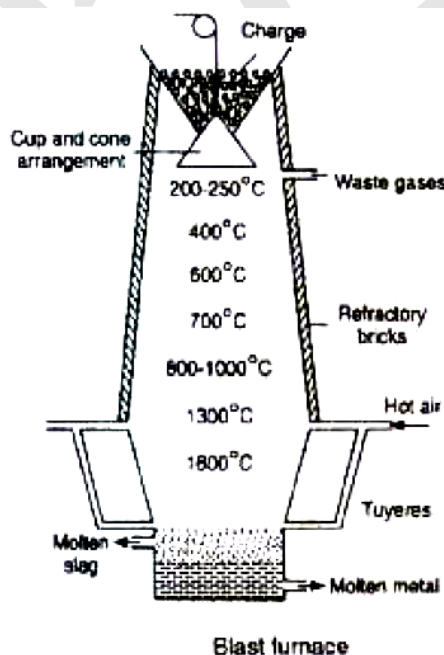
(Fe_2O_3 ore + lime stone + coke) is smelted in blast furnace and following changes take place.

(i) Combustion Zone (155 - 1700°C)

(a) (Combustion zone) a blast of dry preheated air is blown into the furnace from near the bottom of the furnace. Near the bottom, the preheated air comes in contact with the falling coke and combustion of coke into CO_2 takes place.

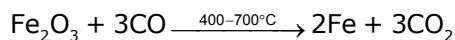


CO_2 produced in the combustion zone rises up and meets with more coke in fusion zone and gets reduced to CO .

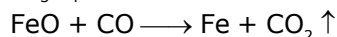
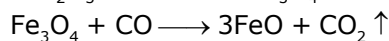
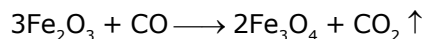


(ii) Reduction zone (250 - 700°C)

Near the top of the furnace (reduction zone), the temperature varies from 250-700°C. Here the oxide ore (Fe_2O_3) is reduced to spongy iron with the help of uprising vapours of CO produced in the zone of fusion.



Actually above Reduction, takes in 3 steps :

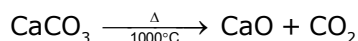


(Spongy iron)

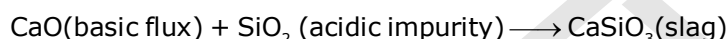
Any Fe_2O_3 which escapes from reduction in reduction zone is reduced in fusion zone.

(iii) Slag formation zone (700-1000°C)

In the middle of the furnace (slag formation zone) where the temperature varies from 700-1000°C, lime stone (CaCO_3) present in the charge decomposes into CaO and CO_2 .



CaO combines with the impurity of SiO_2 and forms a fusible slag of CaSiO_3 . Thus CaO acts as a basic flux.



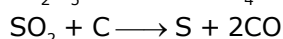
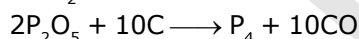
Slag is lighter than the molten iron. It moves down and floats over molten iron. This region where slag is formed is called slag formation zone.

(iv) Fusion Zone (1000 - 1500°C)

Since the reduction of CO_2 to CO is an endothermic reaction (Heat is required), temperature is decreased to about 1500°C. Fe_2O_3 is reduced to Fe which might not have been reduced in the reduction zone.



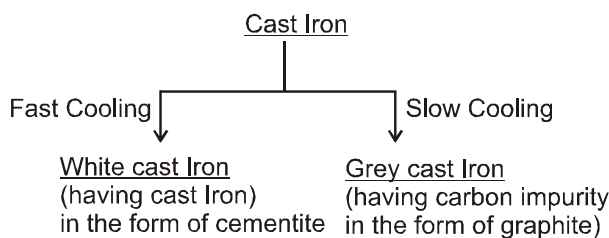
Impurities are also reduced and get mixed up with spongy Iron.



Spongy iron produced in the reduction zone melts here and gets impured in called pig iron, while slag being lighter floats over and thus prevents oxidation of Fe by blast of hot air.

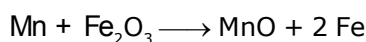
Types of Iron :

1. Cast iron (2% to 5% carbon & other impurity)
2. Steel (0.5% to 2% carbon & other impurity)
3. Wrought iron (< 0.5% carbon & other impurity)

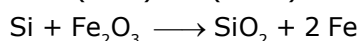


Manufacturing of wrought from cast Iron :

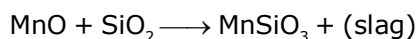
Wrought iron is manufactured from puddling furnace having inner lining of haematite (Fe_2O_3) oxidant for impurities present in cast iron.



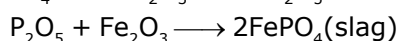
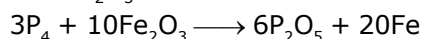
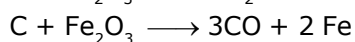
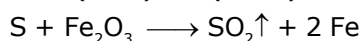
(O.A.) (basic)



(O.A.) (basic)



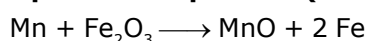
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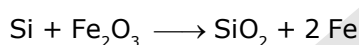
Manufacturing of steel from cast from :

- (i) Bassemerisation (already discussed)
- (ii) Open-Hearth process (Siemen Marthin's process)
- (iii) Electrical furnace process

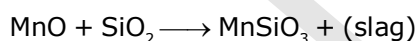
Open hearth process (siemen Mortin's process)



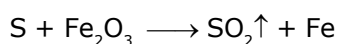
(O.A.) (basic)



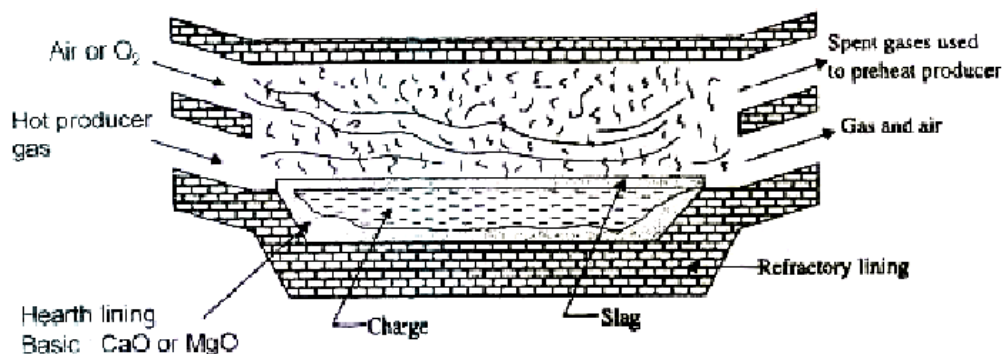
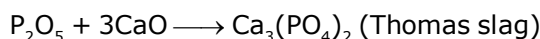
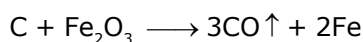
(O.A.) (Acidic)



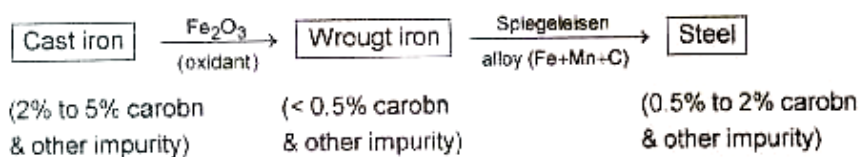
(O.A.) (basic)



(O.A.)



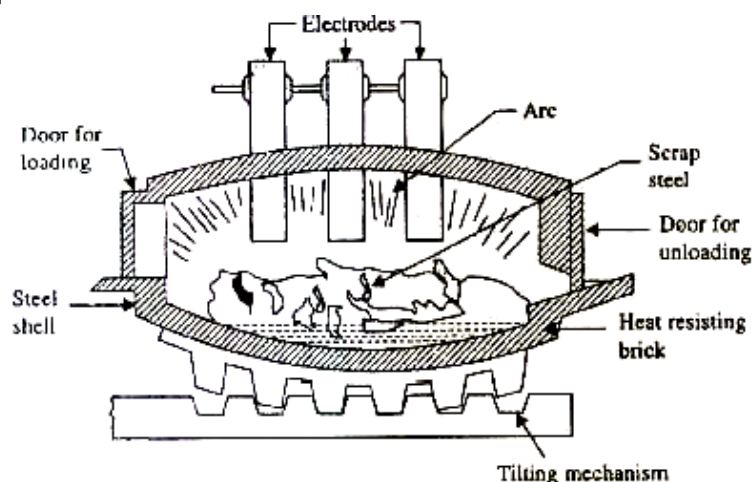
Open hearth furnace for the manufacture steel from cast iron



After adding required amount of spiegeleisen steel is formed.

In this method 2 – 5% iron is also oxidised by air because hearth is open therefore this method is discarded in modern age.

In modern age steel is manufactured by electrical furnace process or by L.D. process. In electrical furnace process heating effect is produced by passing electricity and all chemical reaction are similar to open-hearth process.



Arc furnace (Heroult's furnace) for the manufacture of steel.

Heating Treatment of STEEL

(i) Annealing : Process of heating steel upto redness and then cooling it slowly is called annealing, In this way steel becomes soft, malleable and elastic.

(ii) Quenching : Process of heating steel upto redness and then cooling it suddenly by plunging in into oil or water is called quenching. In this way steel become hard and brittle.

(iii) Tempering : Process of heating quenched steel much below redness and then cooling it slowly is called tempering. In this steel becomes neither so hard nor so brittle.

Surface Treatment of steel :

(i) Case – Hardening : Process of forming hard coating of iron carbide over mild steel by heating it with charcoal is called case – hardening.

(ii) Nitriding : Process of forming hard coating of iron nitride by heating steel with ammonia gas is called nitriding.

7. Zinc :

Ores : Zinc blende ZnS (main ore), Zincite (ZnO), Calamine, ZnCO_3 .

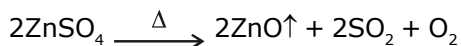
Extraction of zinc from zinc blende :

(A) Crushing and concentration :

The ore is crushed and concentrated by froth floatation process.

(B) Roasting :

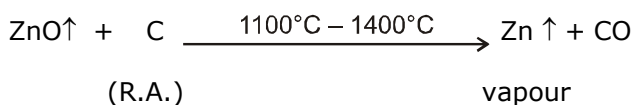
The concentrated ore is roasted in presence of excess of air



ZnSO_4 decomposed at higher temperature

(C) Carbon Reduction (Belgian process) :

Roasted ore is heated with coke in a vertical fire clay retort.



Vapours of zinc are collected by rapid cooling to get zinc spelter (Impure Zn).

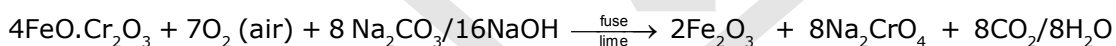
Impure Zn is purified either by **electrolytic refining method** or by **distillation**.

(D) Electrolytic refining :

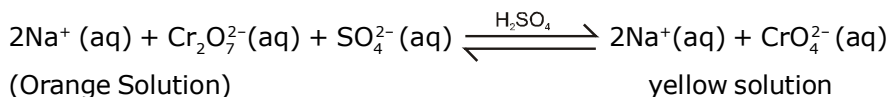
Anode	:	Impure Zn
Cathode	:	Aluminium Electrode
Electrolyte	:	$\text{ZnSO}_4(\text{aq}) + \text{H}_2\text{SO}_4$

*** Extraction of Cr From FeCr_2O_4 ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) Chromite ORE :**

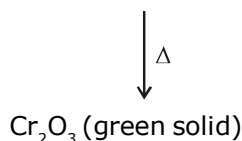
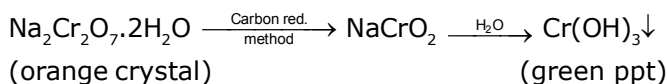
Conc. Step : Chromite ore is concentrated by gravity sep. Method to remove light impurities followed by magnetic sep. method to remove non-magnetic impurities.

Chemical Method to Separate Cr_2O_3 :

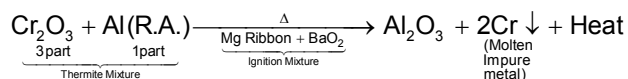
Brown yellow solid
(water insoluble) (water soluble)
↓ Water



↓ Fractional
crystallisation



Al-reduction method : (Goldsmith alumino thermite process)

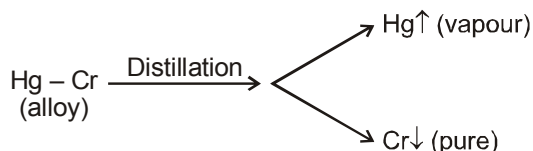


Impure Cr is purified by **electrolytic refining method**.

Anode : Impure chromium

Cathode : Hg-electrode

Electrolyte : $\text{CrCl}_3 + \text{HCl}$

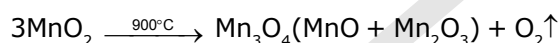


*** Extraction of Mn from MnO_2 (Pyrolusite) :**

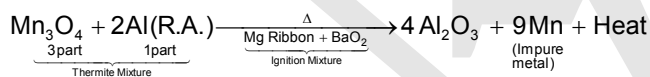
Pyrolusite is concentrated by gravity separation method followed by magnetic separation method to remove non-magnetic impurity.

Calcination :

MnO_2 gives explosive rxn. with Al therefore in this step it is converted into mixed oxide Mn_3O_4 .



Al-reduction method : (Goldsmith alumino thermite process)

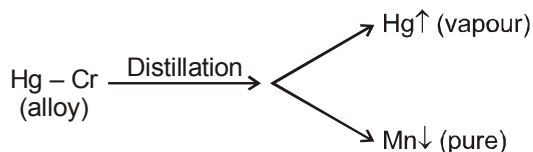


Impure Mn is purified by electrolytic refining method.

Anode : Impure Mn

Cathode : Hg-electrode

Electrolyte : $\text{MnSO}_4 + \text{H}_2\text{SO}_4$



8. Aluminium :

Ores :

(i) Bauxite $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (main ORE) ; Diaspore $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$; Corundum Al_2O_3

(ii) Mica $\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$; Kaolin $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

(iii) Cryolite Na_3AlF_6

Extraction of Al from Bauxite :

Purification of Bauxite :

(i) Baeyer's Method (used for red bauxite containing Fe_2O_3 as impurities)	(ii) Hall's Method (used for red bauxite containing Fe_2O_3 as impurities)	(iii) Serpeck's Method (used for white bauxite containing silica as impurities)
$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \xrightarrow{\Delta} 2\text{NaAlO}_2 + 3\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 \xrightarrow{\text{Fuse}} 2\text{NaAlO}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} + 3\text{C} + \text{N}_2 \xrightarrow{1800^\circ} 2\text{AlN} + 3\text{CO} + 2\text{H}_2\text{O}$
Fe_2O_3 insoluble separated as red mud by filtration	$2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \xrightarrow{60^\circ\text{C}} 2\text{Al}(\text{OH})_3 + \text{Na}_2\text{CO}_3$	$2\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{NH}_3$
$\text{NaAlO}_2 + 2\text{H}_2\text{O} \xrightleftharpoons{\text{H}^+} \text{NaOH} + \text{Al}(\text{OH})_3$		$\text{SiO}_2 + 2\text{C} \xrightarrow{1800^\circ\text{C}} 2\text{CO}\uparrow + \text{Si}\uparrow$
$2\text{Al}(\text{OH})_3 \xrightarrow{\Delta, >1000^\circ\text{C}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	$2\text{Al}(\text{OH})_3 \xrightarrow{\Delta, >1000^\circ\text{C}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$	$2\text{Al}(\text{OH})_3 \xrightarrow{\Delta, >1000^\circ\text{C}} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

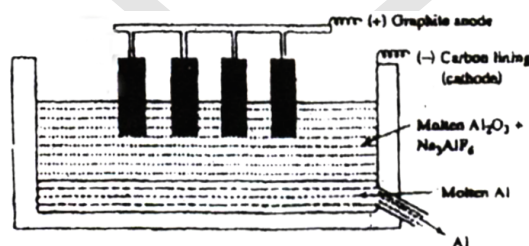
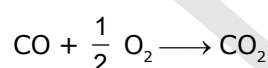
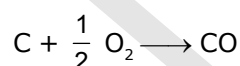
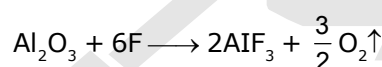
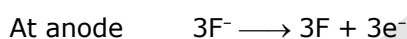
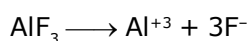
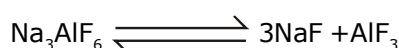
Electrolysis of pure fused Al_2O_3 (Hall - Heroult method)

Cathode - iron tank lined with graphite

Anode - Carbon rods dipped in molten electrolyte

Electrolyte - molten ($20\% \text{Al}_2\text{O}_3 + 60\% \text{Cryolite} + 20\% \text{CaF}_2$) Temp $\approx 1100^\circ\text{C}$

Cryolite lowers the melting point of mixture and makes the molten mix conducting.



Electrolytic cell

Anodes are periodically changed as they are consumed by oxygen liberated at anode.

Electrolytic refining (Hoppe's Method)

Iron box lined with carbon, contains the three molten layers.

Bottom layer : Impure Al as anode

Middle layer : ($\text{Na}_3\text{AlF}_6 + \text{BaF}_2$) Molten electrolyte

Top layer : molten pure Al as cathode.

On passing the current aluminium is deposited at cathode from the middle layer and an equivalent amount is taken from anode (bottom layer) leaving behind the impurities. In this way aluminium obtained is 99.98% pure.

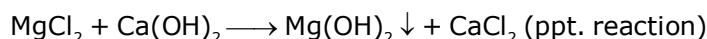
9. Magnesium : (Dow's process)

Ores :

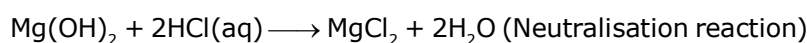
Carnallite $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ (main ore) ; Epsom $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ magnesite MgCO_3 ; Kieserite $\text{MgSO}_4 \cdot \text{H}_2\text{O}$; Dolomite $\text{MgCO}_3 \cdot \text{CaCO}_3$; Kainite $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Mg is also found in Talc, asbestos and chlorophyll)

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) Precipitation of magnesium as magnesium hydroxide by slaked lime :

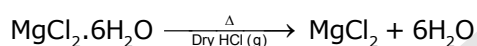


(b) Preparation of hexahydrated magnesium chloride :



The solution on concentration and crystallisation gives the crystals of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

(c) Preparation of anhydrous magnesium chloride :

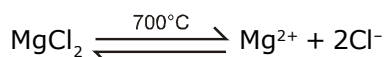


* It is not made anhydrous by simple heating because it gets hydrolysed.



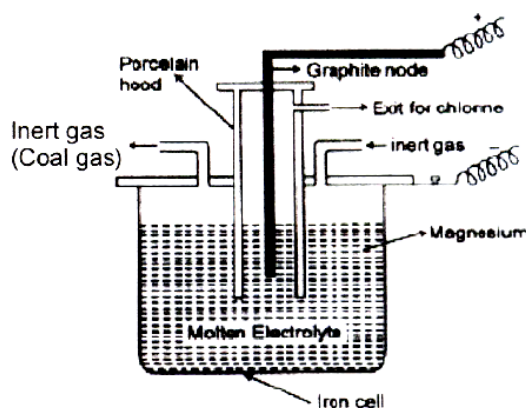
(d) Electrolysis of fused anhydrous MgCl_2 :

Magnesium chloride obtained by any of the above methods is fused and mixed with sodium chloride and calcium chloride in the temperature range of 972 – 1023K. The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.



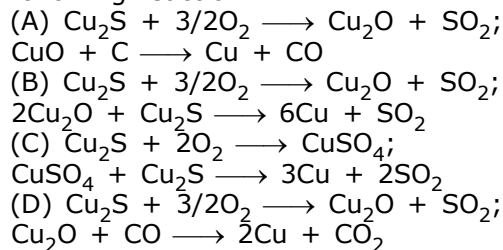
At cathode : $\text{Mg}^{2+} + 2\text{e}^- \longrightarrow \text{Mg(99\% pure)}$;

At anode : $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$



EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. Formation of metallic copper from the sulphide ore in the commercial thermo-metallurgical process essentially involves which one of the following reaction :

**Sol.**

2. $\text{Ag}_2\text{S} + \text{NaCN} + \text{Zn} \longrightarrow \text{Ag}$
 This method of extraction of Ag by complex formation and then its displacement is called :

- (A) Parke's method
 (B) MacArthur–Forest method
 (C) Serpeck method
 (D) Hall's method

Sol.

3. Calcination is the process of heating the ore :
 (A) in inert gas
 (B) in the presence of air
 (C) in the absence of air
 (D) in the presence of CaO and MgO

Sol.

4. Which of the following does not contain Mg :
 (A) magnetite (B) Magnesite
 (C) Asbestos (D) Carnallite

Sol.

5. Match the method of concentration of the ore in column I with the ore in column II and select the correct alternate:

I		II
X magnetic separation		(a) Ag_2S
Y froth floatation		(b) FeCr_2O_4
Z gravity separation		(c) $\text{Al}_2(\text{SiO}_3)_3$
	X Y Z	
(A)	(a) (b) (c)	
(B)	(b) (a) (c)	
(C)	(c) (a) (b)	
(D)	(b) (c) (a)	

Sol.

6. Bessemerization is carried out for
 (I) Fe (II) Cu
 (III) Al (IV) silver
 (A) I, II (B) II, III
 (C) III, IV (D) I, III

Sol.

7. Refining of silver is done by :
 (A) liquation (B) poling
 (C) cupellation (D) van Arkel method

Sol.

8. Which of the following is not used for obtaining Ag
 (A) as a side product in electrolytic refining of copper.
 (B) Parke's process in which Zn is used to extract silver by solvent extraction from molten lead.
 (C) by reaction of silver sulphide with KCN and then reaction of soluble complex with Zn.
 (D) by heating $\text{Na}[\text{Ag}(\text{CN})_2]$

Sol.

9. Blister Cu is about :
(A) 60% Cu (B) 90% Cu
(C) 98% Cu (D) 100% Cu

Sol.

10. Which one of the following is not a method of concentration of ore?
(A) gravity separation
(B) froth floatation process
(C) electromagnetic separation
(D) smelting

Sol.

11. In which of the following isolations no reducing agent is required :
(A) iron from haematite
(B) aluminium from bauxite
(C) mercury from cinnabar
(D) zinc from zinc blends

Sol.

12. Chemical leaching is useful in the concentration of :
(A) copper pyrites (B) bauxite
(C) galena (D) cassiterite

Sol.

13. The element which could be extracted by electrolytic reduction of its oxide dissolved in a high temperature melt is :
(A) sodium (B) magnesium
(C) fluorine (D) aluminium

Sol.

14. Consider the following statements :
Roasting is carried out to :
(i) convert sulphide to oxide and sulphate
(ii) remove water of hydration
(iii) melt the ore
(iv) remove arsenic and sulphur impurities
Of these statements :
(A) (i), (ii) and (iii) are correct
(B) (i) and (iv) are correct
(C) (i), (ii) and (iv) are correct
(D) (ii), (iii) and (iv) are correct

Sol.

15. Iron obtained from blast furnace is :
(A) wrought iron (B) cast iron
(C) pig iron (D) steel

Sol.

16. Which of the following is not an ore :
(A) malacite (B) calamine
(C) stellite (D) cerussite

Sol.

17. Which one of the following statements is not correct :
(A) Nickel forms $\text{Ni}(\text{CO})_4$.
(B) All the transition metals form monometallic carbonyls.
(C) Carbonyls are formed by transition metals.
(D) Transition metals form complexes.

Sol.

18. In the extraction of nickel by Mond process, the metal is obtained by :
 (A) electrochemical reduction
 (B) thermal decomposition
 (C) chemical reduction by aluminium
 (D) reduction by carbon

Sol.

19. B_4C (boron carbide) is used except:
 (A) to extract boron
 (B) As an abrasive for polishing
 (C) For making bullet-proof clothing
 (D) For making diborane

Sol.

20. Froth floatation process is based on:
 (A) Wetting properties of ore particles
 (B) Specific gravity of ore particles
 (C) Magnetic properties of ore particles
 (D) Electrical properties of ore particles

Sol.

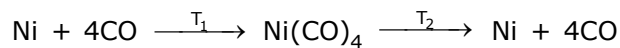
21. When ZnS and PbS minerals are present together, then $NaCN$ is added to separate them in the froth floatation process as a depressant, because
 (A) $Pb(CN)_2$ is precipitated while no effect on ZnS
 (B) ZnS forms soluble complex $Na_2[Zn(CN)_4]$
 (C) PbS forms soluble complex $Na_2[Pb(CN)_4]$
 (D) They cannot be separated by adding $NaCN$

Sol.

22. When copper is purified by electrorefining process, noble metals like Ag and Au are found in
 (A) Cathode mud (B) Electrolytic solution
 (C) Anode mud (D) Over cathode or anode

Sol.

23. Formation of $Ni(CO)_4$ and subsequent its decomposition into Ni and CO (recycled) makes basis of Mond's process



T_1 and T_2 are :

- (A) $100^\circ C$, $50^\circ C$ (B) $50^\circ C$, $100^\circ C$
 (C) $50^\circ C$, $230^\circ C$ (D) $230^\circ C$, $50^\circ C$

Sol.

24. Match column-I (process) with column-II (electrolyte) :

Column-I (process)

- (i) Downs cell
 (ii) Dow sea water process
 (iii) Hall-Heroult

- (iv) Moissan

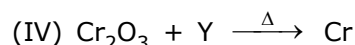
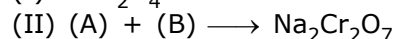
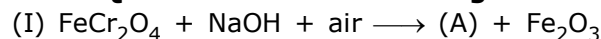
Column-II (electrolyte)

- (W) fused $MgCl_2$
 (X) fused $(Al_2O_3 + Na_3AlF_6 + CaF_2)$
 (Y) fused KHF_2
 (Z) fused $(40\% NaCl + 60\% CaCl_2)$

Choose the correct alternate.

- | | (i) | (ii) | (iii) | (iv) |
|-----|-----|------|-------|------|
| (A) | Z | W | X | Y |
| (B) | X | Y | Z | W |
| (C) | W | Z | X | Y |
| (D) | X | Z | W | Y |

Sol.

Q.No.25 to Q.28 are based on following reactions

25. Compounds (A) and (B) are :

- (A) Na_2CrO_4 , H_2SO_4
 (B) $Na_2Cr_2O_7$, HCl
 (C) Na_2CrO_5 , H_2SO_4
 (D) $Na_4[Fe(OH)_6]$, H_2SO_4

Sol.

26. (X) and (Y) are :

- (A) C and Al (B) Al and C
(C) C in both (D) Al in both

Sol.27. Na_2CrO_4 and Fe_2O_3 are separated by :

- (A) dissolving in conc. H_2SO_4
(B) dissolving in NH_3
(C) dissolving in H_2O
(D) dissolving in dil. HCl

Sol.28. High temperature ($> 1000^\circ\text{C}$) electrolytic reduction is necessary for isolating :

- (A) Al (B) Cu
(C) C (D) F_2

Sol.

29. In froth-floatation process, palm oil functions as :

- (A) activator (B) frother
(C) collector (D) agitator

Sol.

30. Collector are the substances which help in attachment of an ore particle to air bubble in froth. A popular collector used industrially is :

- (A) sodium ethyl xanthate
(B) sodium xenate
(C) sodium pyrophosphate
(D) sodium nitroprusside

Sol.

31. Zone refining is based on the principle of :

- (A) fractional distillation
(B) fractional crystallisation
(C) partition coefficient
(D) chromatographic separation

Sol.

32. Which of the following species is desirable substance in extraction of copper but not in extraction of iron?

- (A) CaSiO_3 (B) FeSiO_3
(C) SiO_2 (D) Coke

Sol.

33. Select incorrect statement regarding silver extraction process

- (A) When the lead-silver alloy is rich in silver, lead is removed by the cupellation process.
(B) When the lead-silver alloy is rich in lead, lead is removed by parke's or pattinson's process.
(C) Zinc forms an alloy with lead, from which lead is separated by distillation
(D) Zinc forms an alloy with silver, from which zinc is separated by distillation.

Sol.

34. Which of the following reaction does not occur in Bessemer's converter?

- (A) $2\text{Cu}_2\text{S} + 5\text{O}_2 \longrightarrow 2\text{CuSO}_4 + 2\text{CuO}$
(B) $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2\uparrow$
(C) $2\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2$
(D) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$

Sol.

35. Dow's process :

- (A) involves purification of copper
- (B) involves extraction of magnesium
- (C) gives metal chloride as product
- (D) gives pure metal as product

Sol.

36. In the cyanide process involving extraction of silver, zinc is used industrially as a(an) :

- (A) oxidising agent
- (B) reducing agent
- (C) solvent
- (D) solvating agent

Sol.

37. Carnallite does not contain :

- (A) K
- (B) Ca
- (C) Mg
- (D) Cl

Sol.

38. During initial treatment, preferential wetting of ore by oil and gangue by water takes place in

- (A) Levigation (gravity separation)
- (B) Froth floatation
- (C) Leaching
- (D) Bessemerisation

Sol.

39. Silica is added to roasted copper ores during extraction in order to remove :

- (A) cuprous sulphide
- (B) ferrous oxide
- (C) ferrous sulphide
- (D) cuprous oxide

Sol.

40. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese :

- (A) gives hardness to steel
- (B) helps the formation of oxides of iron
- (C) can remove oxygen and sulphur
- (D) can show highest oxidation state of +7

Sol.

41. Among the following statements, the incorrect one is :

- (A) calamine and siderite are carbonate ores
- (B) argentite and cuprite are oxide ores
- (C) zinc blende and pyrites are sulphide ores
- (D) malachite and azurite are ores of copper

Sol.

42. In the commercial electrochemical process for aluminium extraction the electrolyte used is :

- (A) $\text{Al}(\text{OH})_3$ in NaOH solution
- (B) an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$
- (C) a molten mixture of Al_2O_3 , Na_3AlF_6 and CaF_2
- (D) a molten mixture of $\text{AlO}(\text{OH})$ and $\text{Al}(\text{OH})_3$

Sol.

43. Match column-I with column-II and select the correct answer using the codes given below the lists:

Column-I

- (a) Van Arkel method
(b) Solvay process
(c) Cupellation
(d) Poling

Column-II

- (1) Manufacture of caustic soda
(2) Purification of titanium
(3) Manufacture of Na_2CO_3
(4) Purification of copper
(5) Refining of silver

Codes:	a	b	c	d
(A)	2	1	3	4
(B)	4	3	2	5
(C)	2	3	5	4
(D)	5	1	3	4

Sol.

44. Blister copper is refined by stirring molten impure metal with green logs of wood because such a wood liberates hydrocarbon gases (like CH_4). This process X is called _____ and the metal contains impurities of Y is _____.
(A) X = cupellation, Y = CuO_2
(B) X = poling, Y = Cu_2O
(C) X = poling, Y = CuO
(D) X = cupellation, Y = CuO

Sol.

45. Select the correct statement :
(A) Magnetite is an ore of manganese
(B) Pyrolusite is an ore of lead
(C) Siderite is carbonate ore of iron
(D) FeS_2 is rolled gold

Sol.

46. Three most occurring elements in the earth crust are :
(A) O, Si, Al (B) Si, O, Fe
(C) Fe, Ca, Al (D) Si, O, N

Sol.

47. An ore containing the impurity of FeCr_2O_4 is concentrated by :
(A) magnetic-separation
(B) gravity separation
(C) froth-floatation method
(D) electrostatic method

Sol.

48. A piece of steel is heated until redness and then plunged into cold water or oil. This treatment of steel makes it :
(A) soft and malleable
(B) hard but not brittle
(C) more brittle
(D) hard and brittle

Sol.

49. Give the correct order of initials T or F for following statements. Use T if statement is true and F if it is false:
(i) Cu metal is extracted from its sulphide ore by reduction of Cu_2O with FeS .
(ii) An ore of Tin containing FeCrO_4 is concentrated by magnetic separation method.
(iii) Auto reduction process is used in the extraction Cu & Hg.
(iv) Cassiterite and Rutile are oxide ores of the metals.
(A) TFFT (B) TTFT
(C) FTTT (D) FFFT

Sol.

50. In the extraction of aluminium :

Process X : applied for red bauxite to remove iron oxide (chief impurity)

Process Y : (Serpeck's process) : applied for white bauxite to remove Z (chief impurity) then, process X and impurity Z are :

- (A) X = Hall and Heroult's process and Z = SiO_2
 (B) X = Baeyer's process and Z = SiO_2
 (C) X = Serpeck's process and Z = iron oxide
 (D) X = Baeyer's process and Z = iron oxide

Sol.

51. Which of the following statement(s) is/are incorrect?

- (A) Liquation is applied when the metal has low melting point than that of impurities.
 (B) Presence of carbon in steel makes it hard due to formation of Fe_3C called cementite.
 (C) Less reactive metals like Hg, Pb and Cu are obtained by auto reduction of their sulphide or oxide ores.
 (D) Amalgamation method of purification cannot be applied for Au and Ag.

Sol.

52. Si and Ge used for semiconductors are required to be of high purity and hence purified by :

- (A) zone-refining
 (B) electrorefining
 (C) Van-Arkel's process
 (D) cupellation process

Sol.

53. In electrorefining of metals anode and cathode are taken as thick slab of impure metal and a strip of pure-metal respectively while the electrolyte is solution of a complex metal salt. This method cannot be applied for the refining of :

- (A) Copper (B) Sodium
 (C) Aluminium (D) Zinc and Silver

Sol.

54. Select the correct statement :

- (A) Black jack is ZnS .
 (B) Sulphide ores are concentrated by floatation method.
 (C) Parke's process is based on distribution principle.
 (D) All are correct.

Sol.

55. The metal of which, its property of formation of volatile complex is taken in account for its extraction is :

- (A) Cobalt (B) Nickel
 (C) Vanadium (D) Iron

Sol.

56. Match List-I with List-II

List-I (Property)

- I Explosive
 II Self-reduction
 III Magnetic material
 IV Verdigris

List-II (Element/compound)

- A Cu
 B Fe_3O_4
 C $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2$
 D $\text{Pb}(\text{NO}_3)_2$
 (A) I-A, II-B, III-C, IV-D
 (B) I-D, II-A, III-B, IV-C
 (C) I-D, II-B, III-A, IV-C
 (D) I-C, II-A, III-B, IV-D

Sol.

57. A metal has a high concentration into the earth crust and whose oxides cannot be reduced by carbon. The most suitable method for the extraction of such metal is :
- (A) Alumino thermite process
 - (B) Electrolysis process
 - (C) Van-Arkel's process
 - (D) Cupellation

Sol.

58. The process, which does not use a catalyst is
- (A) Contact process
 - (B) Thermite process
 - (C) Ostwald's process
 - (D) Haber's process

Sol.

59. Refractory materials are generally used in furnaces because :
- (A) they are chemically inert
 - (B) they can withstand high temperature
 - (C) they do not contain impurities
 - (D) they decrease melting point of ore

Sol.

60. % of silver in 'german silver' is :
- (A) 0
 - (B) 80
 - (C) 90
 - (D) 10

Sol.

61. Modern method of steel manufacturing is :
- (A) open hearth process
 - (B) L. D. Process
 - (C) Bessemerization
 - (D) Cupellation

Sol.

62. When an impurity in a metal has greater affinity for oxygen and is more easily oxidises than the metal itself. Then, the metal is refined by :
- (A) cupellation
 - (B) zone-refining
 - (C) distillation
 - (D) electrolytic process

Sol.

63. The chemical process in the production of steel from haematite ore involve :
- (A) Reduction
 - (B) Oxidation
 - (C) Reduction followed by oxidation
 - (D) oxidation followed by reduction

Sol.

64. "Fool's gold" is :
- (A) iron pyrites
 - (B) horn silver
 - (C) copper pyrites
 - (D) bronze

Sol.

65. During electrolytic reduction of alumina, two auxiliary electrolytes X and Y are added to increase the electrical conductance and lower the temperature of melt in order to making fused mixture very conducting. X and Y are :
- (A) cryolite and flourspar
(B) cryolite and alum
(C) alum and flourspar
(D) flourspar and bauxite

Sol.

66. For extraction of sodium from NaCl, the electrolytic mixture NaCl + KCl + CaCl₂ is used. During extraction process, only sodium is deposited on cathode but K and Ca do not because :
- (A) Na is more reactive than K and Ca
(B) Na is less reactive than K and Ca
(C) NaCl is less stable than Na₃AlF₆ and CaCl₂
(D) the discharge potential of Na⁺ is more than that of K⁺ and Ca²⁺ ions.

Sol.

67. A solution of Na₂SO₄ in water is electrolysed using inert electrodes. The products at cathode and anode are respectively
- (A) O₂ ; H₂ (B) O₂ ; Na
(C) H₂ ; O₂ (D) O₂ ; SO₂

Sol.

68. Which of the following statements is correct regarding the slag formation during the extraction of a metal like copper or iron :
- (A) The slag is lighter and lower melting than the metal.
(B) The slag is heavier and lower melting than the metal.
(C) The slag is lighter and higher melting than the metal.
(D) The slag is heavier and higher melting than the metal.

Sol.

69. Among the following groups of oxides, the group containing oxides that cannot be reduced by C to give the respective metal is :
- (A) CaO and K₂O (B) Fe₂O₃ and ZnO
(C) Cu₂O and SnO₂ (D) PbO and Pb₃O₄

Sol.

70. The beneficiation of the sulphide ores is usually done by :
- (A) Electrolysis
(B) Smelting process
(C) Metal displacement method
(D) Froth floatation method

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Hoop's process of purification of aluminium involves formation of layers during electrolysis. It involves :

(A) the three layers have same densities but different materials.
 (B) the three layers have different densities.
 (C) the upper layer is of pure aluminium which acts as a cathode.
 (D) the bottom layer is of impure aluminium which acts as an anode and middle layer consists of cryolite and BaF_2 .

Sol.

2. Metallurgical process of zinc involves roasting of zinc sulphide followed by reduction. Metallic zinc distills over as it is volatile and impurities like Cu, Pd and Fe gets condensed. The crude metal obtained is called spelter which may be purified by :

(A) electrolysis process (B) fractional distillation
 (C) polling (D) heating with iodide

Sol.

3. Calcination and roasting process of reduction of ores to their oxides are beneficial :

(A) to convert ores into porous form so that their reduction becomes easier.
 (B) as volatile impurities like P, As, Sb, S are removed.
 (C) as organic impurities are removed.
 (D) as the ores are converted into oxide form which makes the reduction easier.

Sol.

4. In the extraction of copper, the reaction which takes place in Bessemer converter is :

(A) $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2\uparrow$
 (B) $\text{CuFeS}_2 + \text{O}_2 \longrightarrow \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2\uparrow$
 (C) $2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2\uparrow$
 (D) $2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2$

Sol.

5. Extraction of silver from argentiferous lead (Pb + Ag) involves :

(A) distillation method
 (B) cupellation
 (C) froth flotation method
 (D) treatment with NaCl

Sol.

6. In the manufacturing of metallic sodium by fused salt-electrolysis method (Down's process), small amount of CaCl_2 that added is known as auxiliary electrolyte and is used to :

(A) improve the electrical conductance
 (B) decrease the melting point of NaCl
 (C) stabilise the metallic sodium
 (D) increase the temperature of electrolysis

Sol.

7. Metal(s) which does/do not form amalgam is/are :

(A) Fe (B) Pt
 (C) Zn (D) Au

Sol.

8. Auto reduction process is used in extraction of

- (A) Cu (B) Hg
(C) Al (D) Fe

Sol.

9. Zone refining is used for purification of :

- (A) Ge (B) Si
(C) Ga (D) Se

Sol.

10. Which of the following process(es) are used for purification of Bauxite ore?

- (A) Hall's process (B) Serpeck's process
(C) Baeyer's process (D) Mond's process

Sol.

11. Metals which can be extracted by smelting process :

- (A) Pb (B) Fe
(C) Zn (D) Mg

Sol.

12. Common impurities present in Bauxite are :

- (A) CuO (B) ZnO
(C) Fe₂O₃ (D) SiO₂

Sol.

13. Which of the following reduction reactions are actually employed in commercial extraction of metals?

- (A) $\text{Fe}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$
(B) $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$
(C) $2\text{Na}[\text{Au}(\text{CN})_2] + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Au}$
(D) $\text{Cu}_2\text{S} + \text{Pb} \longrightarrow \text{Cu} + \text{PbS} \downarrow$

Sol.

14. Which of the following cannot be obtained by electrolytic reduction of their compounds in aqueous solution?

- (A) Barium (B) Cadmium
(C) Potassium (D) nickel

Sol.

15. Which of the following ores is(are) concentrated by froth floatation?

- (A) haematite
(B) galena
(C) copper pyrite
(D) azurite

Sol.

16. Which of the following statement(s) is/are common between roasting and sintering?

- (A) Both require heating of the ore.
(B) Both involve burning away of organic matter.
(C) Both the process cause partial fusion of ore, resulting in bigger lumps.
(D) Both are performed only for sulphide ores.

Sol.

17. Which of the following reaction(s) occur during calcination?

- (A) $\text{CaCO}_3 \longrightarrow \text{CaO} + \text{CO}_2$
(B) $4\text{FeS}_2 + 11\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2$
(C) $2\text{Al}(\text{OH})_3 \longrightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
(D) $\text{CuS} + \text{CuSO}_4 \longrightarrow 2\text{Cu} + 2\text{SO}_2$

Sol.

18. Roasting is usually performed in :

- (A) Blast furnace
(B) reverberatory furnace
(C) Bessemer's converter
(D) electric furnace

Sol.

19. Which of the following is(are) sulphide ores?

- (A) Argentite
(B) Galena
(C) Anglesite
(D) Copper glance

Sol.

20. Which of the following is(are) regarded as iron ores?

- (A) Haematite
(B) Magnetite
(C) Limonite
(D) Copper pyrites

Sol.

21. Which of the following employ downward movement of ore due to gravity?

- (A) Gravity separation
(B) Froth floatation
(C) Blast furnace
(D) Bessemer's coverter

Sol.

22. Calcium silicate slag formed in extraction of iron

- (A) prevents the reoxidation of molten iron.
(B) catalyses the combustion of carbon.
(C) reduces CO_2 to CO at the bottom of the furnace.
(D) is used in cement industry.

Sol.

23. Amphoteric nature of aluminium is employed in which of the following process for extraction of aluminium?

- (A) Baeyer's process
(B) Hall's process
(C) serpeck's process
(D) Dow's process

Sol.

24. Noble metal(s) which are commercially extracted by cyanide process is(are) :

- (A) copper (B) silver
(C) gold (D) mercury

Sol.

25. Carbon reduction method is employed for commercial extraction of :

- (A) haematite
(B) cassiterite
(C) iron pyrite
(D) corundum

Sol.

26. The chief reaction(s) occurring in blast furnace during extraction of iron from haematite is(are)

- (A) $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
- (B) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
- (C) $\text{Fe}_2\text{O}_3 + \text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
- (D) $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$

Sol.

27. Which of the following are true for electrolytic extraction of aluminium :

- (A) cathode material contains graphite
- (B) anode material contains graphite
- (C) cathode reacts away forming CO_2
- (D) anode reacts away forming CO_2

Sol.

28. During extraction of copper, it is obtained in the form of molten matte. Which of the following is not true?

- (A) matte is further treated in Bessemer's converter.
- (B) molten matte is electrolysed.
- (C) It is treated with a blast of air and sand.
- (D) It is dissolved in CuSiF_6 and crystallised.

Sol.

29. Which of the following ores is(are) concentrated industrially by froth floatation?

- (A) Copper pyrites
- (B) Galena
- (C) Dolomite
- (D) Carnallite

Sol.

30. Which of the following is true for calcination of a metal ore?

- (A) It makes the ore more porous.
- (B) The ore is heated to a temperature when fusion just begins.
- (C) Hydrated salts lose their water of crystallisation.
- (D) Impurities of S, As and Sb are removed in the form of their volatile oxides.

Sol.

31. The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is :

- (A) as a catalyst.
- (B) to make the fused mixture very conducting.
- (C) to lower the temperature of the melt.
- (D) to decrease the rate of oxidation of carbon at the anode.

Sol.

32. The difference(s) between roasting and calcination is(are) :

- (A) roasting is highly endothermic while calcination is not.
- (B) partial fusion occurs in calcination but not in roasting.
- (C) calcination is performed in limited supply of air but roasting employs excess air.
- (D) combustion reactions occur in roasting but not in calcination.

Sol.

33. Leaching is used for the concentration of :

- (A) Red bauxite
- (B) Haematite
- (C) Gold Ore
- (D) Silver Ore

Sol.

34. The correct statements are :

- (A) generally the calcination and roasting is done in blast furnace.
- (B) the sandy and rocky materials associated with ore are called matrix.
- (C) froth floatation process is suitable for sulphide ores.
- (D) substance that reacts with gangue to form fusible mass is called slag.

Sol.

35. Poling is employed in refining of :

- (A) iron
- (B) copper
- (C) tin
- (D) lead

Sol.

36. Which of the following reaction is not occur in blast furnace during extraction of iron :

- (A) $\text{CaO} + \text{SiO}_2 \longrightarrow \text{CaSiO}_3$
- (B) $\text{Fe}_2\text{O}_3 + 3\text{CO} \longrightarrow 2\text{Fe} + 3\text{CO}_2$
- (C) $\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_3$
- (D) $\text{FeO} \longrightarrow \text{Fe} + 1/2\text{O}_2$

Sol.

37. Match the following choosing one item from column X and the appropriate item from column Y.

X

- (A) Al
- (B) Cu
- (C) Mg
- (D) Zn

Y

- (P) Calamine
- (Q) Cryolite
- (R) Malachite
- (S) carnallite

Sol.

EXERCISE – III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. In the aluminothermite process, Al acts as :
 (A) An oxidising agent (B) A flux
 (C) A reducing agent (D) A solder

Sol.

2. The process of the isolation of a metal by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called :
 (A) hydrometallurgy
 (B) electrometallurgy
 (C) zone refining
 (D) electrorefining

Sol.

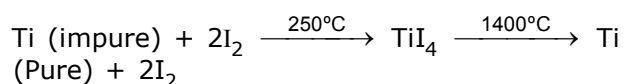
3. Carbon cannot be used in the reduction of Al_2O_3 because:
 (A) It is an expensive proposition
 (B) The enthalpy of formation of CO_2 is more than that Al_2O_3
 (C) Pure carbon is not easily available
 (D) The enthalpy of formation of Al_2O_3 is too high

Sol.

4. Froth floatation process for concentration of ores is an illustration of the practical application of :
 (A) Adsorption (B) Absorption
 (C) Coagulation (D) Sedimentation

Sol.

5. Which process of purification is represented by the following equation :



- (A) Cupellation (B) Poling
 (C) Van-Arkel process
 (D) Zone refining

Sol.

6. Mercury is purified by :
 (A) Passing through dilute HNO_3
 (B) Distillation
 (C) Distribution
 (D) Vapour phase refining

Sol.

7. Which of the following ore and metal are correctly matched:

Ore	Metal
(A) Carnallite	Zinc.
(B) Calamine	Titanium
(C) Ilmenite	Magnesium
(D) Chalcopyrite	Copper

Sol.

8. Which of the following metal is correctly matched with its ore :

Metal	Ore
(A) Zinc	Calamine
(B) Tin	Azurite
(C) Magnesium	Cassiterite
(D) Silver	Ilmenite

Sol.

9. Which of the following employ(s) thermal decomposition of volatile iodide compounds?
 (A) Thermite process
 (B) Hall's process
 (C) Van-Arkel's process
 (D) Mond's process

Sol.

10. The method of zone refining of metals is based on the principle of :
 (A) Greater mobility of the pure metal than that of impurity.
 (B) Higher melting point of impurity than that of the pure metal.
 (C) Greater noble character of the solid metal than that of the impurity.
 (D) Greater solubility of the impurity in the molten state than in the solid.

Sol.

11. Railway wagon axles are made by heating iron rods embedded in charcoal powder. This process is known as :
 (A) Sherardising (B) Annealing
 (C) Tempering (D) Case hardening

Sol.

12. In the extraction of copper from its sulphide ore the metal is formed by the reduction of Cu_2O with:
 (A) FeS (B) CO
 (C) Cu_2S (D) SO_2

Sol.

13. Carnallite on electrolysis gives :
 (A) Ca and Cl_2 (B) Na and CO_2
 (C) Al and Cl_2 (D) Mg and Cl_2

Sol.

14. Among the following statements, the incorrect one is :
 (A) calamine and siderite are carbonates
 (B) Argentite and cuperite are oxides
 (C) Zinc blende and iron pyrites are sulphides
 (D) Malachite and azurite are ores of copper

Sol.

15. Match column-I and column-II and select the correct answer using the codes given below the lists:

Column-I

- (I) Cyanide process
 (II) Floatation process
 (III) Electrolytic reduction
 (IV) Zone refining

Column-II

- (1) Ultrapure Ge
 (2) Dressing of HgS
 (3) Extraction of Al
 (4) Extraction of Au
 (A) I-(3) II-(1), III-(4), IV-(2)
 (B) I-(4) II-(2), III-(3), IV-(1)
 (C) I-(3) II-(2), III-(4), IV-(1)
 (D) I-(4) II-(1), III-(3), IV-(2)

Sol.

16. Match column-I with column-II and select the correct answer using the codes given below :

Column-I (Metals)

- (I) Iron & copper
 (II) Zirconium & Titanium
 (III) Lead & Tin
 (IV) Copper & Tin

Column-II (Method used for refining)

- (P) Poling
 (Q) Bessemerisation
 (R) Van-Arkel
 (S) Liquation

	(I)	(II)	(III)	(IV)
(A)	P	S	R	Q
(B)	Q	S	R	P
(C)	P	R	S	Q
(D)	Q	R	S	P

Sol.

Question No. 17 to 30**Assertion-Reason :**

- (A) If both **Assertion** and **Reason** are true and **Reason** is the correct explanation of **Assertion**.
 (B) If both **Assertion** and **Reason** are true and **Reason** is not the correct explanation of **Assertion**.
 (C) If **Assertion** is true and **Reason** is false.
 (D) If **Assertion** is false and **Reason** is true.

- | | |
|---|---|
| 17. Assertion : Sulphide ores are concentrated by froth floatation process.
Reason : Pine oil acts as a frothing agent in froth floatation process.
Sol. | Sol. |
| 18. Assertion : Platinum and gold occur in native state in nature.
Reason : Platinum and gold are noble metals.
Sol. | 24. Assertion : Titanium is purified by Van-Arkel method.
Reason : Ti reacts with I_2 to form TiI_4 which decomposes at 1700 K to give pure Ti.
Sol. |
| 19. Assertion : Wolframite impurities are separated from cassiterite by electromagnetic separation.
Reason : Cassiterite being magnetic is attracted by the magnet and forms a separate heap.
Sol. | 25. Assertion : CuO can be reduced by C, H_2 as well as Co
Reason : CuO is basic oxide.
Sol. |
| 20. Assertion : In smelting, roasted ore is heated with powdered coke in presence of a flux.
Reason : Oxides are reduced to metals by C or CO. Impurities are removed as slag.
Sol. | 26. Assertion : Alkali metals cannot be prepared by the electrolysis of aq. $MgCl_2$.
Reason : The reduction potential of Mg^{2+} is much lower than that of H^+ .
Sol. |
| 21. Assertion : Al is used as a reducing agent in aluminothermy.
Reason : Al has a lower melting point than Fe, Cr and Mn.
Sol. | 27. Assertion : Magnesium can be prepared by the electrolysis of aq. $MgCl_2$.
Reason : The reduction potential of Mg^{2+} is much lower than that of H^+ .
Sol. |
| 22. Assertion : Lead, tin and bismuth are purified by liquation method.
Reason : Lead, tin and bismuth have low m.p. as compared to impurities.
Sol. | 28. Assertion : Titanium can be purified by Van-Arkel process.
Reason : TiI_4 is a volatile, stable compound.
Sol. |
| 23. Assertion : Wolframite impurity is separated from SnO_2 by magnetic separation.
Reason : Tin stone is ferromagnetic, therefore attracted by magnet. | 29. Assertion : Magnesite and quick lime are used as basic flux.
Reason : MgO and CaO can withstand very high temperatures.
Sol. |
| | 30. Assertion : Nickel is purified by the thermal decomposition of nickel tetracarbonyl.
Reason : Nickel is a transitional element.
Sol. |

EXERCISE – IV**PREVIOUS YEARS****LEVEL – I****JEE MAIN**

1. The metal extracted by leaching with cyanide is : **[AIEEE-2002]**

(A) Mg (B) Ag
(C) Cu (D) Na

Sol.

2. When the sample of Cu with Zn impurity is to be purified by electrolysis, the appropriate electrodes are : **[AIEEE-2002]**

Cathode **Anode**
(A) pure Zn pure Cu
(B) impure sample pure Cu
(C) impure Zn impure sample
(D) pure copper impure sample

Sol.

3. Aluminium is industrially prepared by - **[AIEEE-2002]**

(A) Fused cryolite
(B) Bauxite ore
(C) Alumina
(D) Alumina mixed with molten cryolite

Sol.

4. The substance not likely to contain CaCO_3 is - **[AIEEE-2003]**

(A) Sea shells
(B) Dolomite
(C) A marble statue
(D) Calcined gypsum

Sol.

5. Which one of the following ores is best concentrated by froath-flotation method ? **[AIEEE-2004]**

(A) Magnetite (B) Cassiterite
(C) Galena (D) Malachite

Sol.

6. During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud'. These are - **[AIEEE-2005]**

(A) Pb and Zn (B) Sn and Ag
(C) Fe and Ni (D) Ag and Au

Sol.

7. Heating mixture of Cu_2O and Cu_2S will give - **[AIEEE-2005]**

(A) $\text{Cu} + \text{SO}_3$ (B) $\text{Cu} + \text{SO}_2$
(C) Cu_2SO_3 (D) $\text{CuO} + \text{CuS}$

Sol.

8. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly ? **[AIEEE-2008]**

(A) CO_2 is thermodynamically more stable than CS_2
(B) Metal sulphides are less stable than the corresponding oxides
(C) CO_2 is more volatile than CS_2
(D) Metal sulphides are thermodynamically more stable than CS_2

Sol.

LEVEL – II

JEE ADVANCED

1. In the commercial electrochemical process for aluminium extraction, the electrolyte used as :
- (A) Al(OH)_3 in NaOH solution
 (B) an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$
 (C) a molten mixture of Al_2O_3 and Na_3AlF_6
 (D) a molten mixture of AlO(OH) and Al(OH)_3

[JEE 1999]

Sol.

2. The chemical process in the production of steel from haematite ore involve:

[JEE 2000 Qualifying]

- (A) Reduction
 (B) Oxidation
 (C) Reduction followed by oxidation
 (D) Oxidation followed by reduction

Sol.

3. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out :

[JEE 2000 Qualifying]

- (A) in the presence of NaCl
 (B) in the presence of fluorite
 (C) in the presence of cryolite which forms a melt with lower melting temperature.
 (D) in the presence of cryolite which forms a melt with higher melting temperature.

Sol.

4. The chemical composition of "slag" formed during the smelting process in the extraction of copper is :

[JEE 2001 Qualifying]

- (A) $\text{Cu}_2\text{O} + \text{FeS}$ (B) FeSiO_3
 (C) CuFeS_2 (D) $\text{Cu}_2\text{S} + \text{FeO}$

Sol.

5. Which of the following processes is used in extractive metallurgy of magnesium?

[JEE 2002 Qualifying]

- (A) Fused salt electrolysis
 (B) Self reduction
 (C) Aqueous solution electrolysis
 (D) Thermite reduction

Sol.

6. In the process of extraction of gold,

Roasted gold ore + $\text{CN}^- + \text{H}_2\text{O} \xrightarrow{\text{O}_2} [\text{X}] + \text{OH}^-$
 $[\text{X}] + \text{Zn} \longrightarrow [\text{Y}] + \text{Au}$ Identify the complexes [X] and [Y] :

[JEE 2003 Qualifying]

- (A) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
 (B) $\text{X} = [\text{Au}(\text{CN})_4]^{3-}$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$
 (C) $\text{X} = [\text{Au}(\text{CN})_2]^-$, $\text{Y} = [\text{Zn}(\text{CN})_6]^{4-}$
 (D) $\text{X} = [\text{Au}(\text{CN})_4]^-$, $\text{Y} = [\text{Zn}(\text{CN})_4]^{2-}$

Sol.

7. The methods chiefly used for the extraction of lead and tin from their ores are respectively :

[JEE 2004]

- (A) self reduction and carbon reduction
(B) self reduction and electrolytic reduction
(C) carbon reduction and self reduction
(D) cyanide process and carbon reduction

Sol.

8. Which ore contains both iron and copper?

[JEE 2004]

- (A) Cuprite (B) Chalcocite
(C) Chalcopyrite (D) Malachite

Sol.

9. Extraction for zinc from zinc blende is achieved by :

[JEE 2007]

- (A) electrolytic reduction
(B) roasting followed by reduction with carbon
(C) roasting followed by reduction with another metal
(D) roasting followed by self-reduction

Sol.

10. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCl in the presence of :

[JEE 2008]

- (A) nitrogen (B) oxygen
(C) carbon dioxide (D) argon

Sol.

Paragraph for Question 11 to 13

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcantite ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) atacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$). However, 80% of the world copper production comes from the ore chalcopyrite (CuFeS_2). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. [JEE 2010]

11. Partial roasting of chalcopyrite produces

- (A) Cu_2S and FeO
(B) Ca_2O and FeO
(C) CaS and Fe_2O_3
(D) Cu_2O and Fe_2O_3

Sol.

12. Iron is removed from chalcopyrite as

- (A) FeO (B) FeS
(C) Fe_2O_3 (D) FeSiO_3

Sol.

13. In self-reduction, the reducing species is

- (A) S (B) O^{2-}
(C) S^{2-} (D) SO_2

Sol.

14. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are

- (A) II, III in haematite and III in magnetite
(B) II, III in haematite and II in magnetite
(C) II in haematite and II, III in magnetite
(D) III in haematite and II, III in magnetite

[JEE 2011]

Sol.

15. Extraction of metal from the ore **cassiterite** involves

[JEE 2011]

- (A) Carbon reduction of an oxide ore
(B) Self-reduction of a sulphide ore
(C) removal of copper impurity
(D) removal of iron impurity

Sol.

Subjective

16. Answer the following questions briefly :

[JEE 1987]

- (i) What is the actual reducing agent of haematite in blast furnace?
(ii) Give the equations for the recovery of lead from galena by air reduction.
(iii) Why is sodium chloride added during electrolysis of fused anhydrous magnesium chloride?
(iv) Why copper metal is not used for the recovery of metallic silver from complex $[Ag(CN)_2]^-$ explain.
(v) Why is chalcocite roasted and not calcinated during recovery of copper?

Sol.

17. Give balanced equations for the following :

"Extraction of silver from silver glance by cyanide process."

[JEE 1998]

Sol.

18. Write balanced equation for "the extraction of copper from copper pyrites by self reduction."

[JEE 1990]

Sol.

19. Give briefly the isolation of magnesium from sea water by the Dow's process. Give equations for the steps involved. **[JEE 1993]**

Sol.

20. Give reasons for the following : **[JEE 1994]**

"Although aluminium is above hydrogen in the electrochemical series, it is stable in air and water."

Sol.

21. When the ore haematite is burnt in air with coke around 2000°C alongwith lime, the process not only produces steel but also produces a silicate slag, that is useful in making building materials such as cement. Discuss the same and show through balanced chemical equation.

[JEE 1998]

Sol.

22. Write the chemical reactions involved in the extraction of metallic silver from argentite.

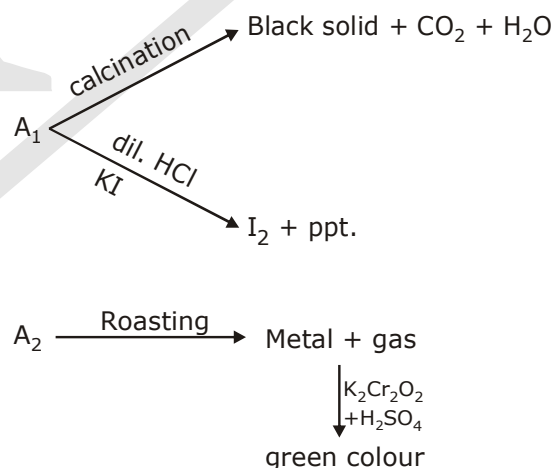
[JEE main 2000]

Sol.

23. Write down reactions involved in the extraction of Pb. What is the oxidation number of lead in litharge? **[JEE main 2003]**

Sol.

24. A_1 and A_2 are two ores of metal M. A_1 on calcination gives black precipitate, CO_2 and water. **[JEE 2004]**



Sol.

Match the column :

25. Match the extraction processes listed in column-I with metals listed in column-II. [JEE 2006]

Column-I

- (A) Self reduction
(B) Carbon reduction
(C) Complex formation and displacement by metal
(D) Decomposition of iodide

Column-II

- (P) Lead
(Q) Silver
(R) Copper
(S) Boron

Sol.

26. Match the conversions in Column-I with the type(s) of reaction(s) given in Column-II. Indicate your answer by darkening the appropriate bubbles of the 4×4 matrix given in the ORS.

Column-I**[JEE 2008]**

- (A) $\text{PbS} \longrightarrow \text{PbO}$
(B) $\text{CaCO}_3 \longrightarrow \text{CaO}$
(C) $\text{ZnS} \longrightarrow \text{Zn}$
(D) $\text{Cu}_2\text{S} \longrightarrow \text{Cu}$

Column-II

- (P) Roasting
(Q) Calcination
(R) Carbon reduction
(S) Self reduction

Sol.**Fill in the blanks :**

27. In extractive metallurgy of zinc partial fusion of ZnO with coke is called _____ and reduction of the ore to the molten metal is called _____ (smelting, calcining, roasting, sintering) [JEE 1988]

Sol.

28. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agent used are [JEE 2012]

- (A) O_2 and CO respectively
(B) O_2 and Zn dust respectively
(C) HNO_3 and Zn dust respectively
(D) HNO_3 and CO respectively

Sol.

29. Sulfide ores are common of the metals

[JEE 2013]

- (A) Ag , Cu and Pb
(B) Ag , Cu and Sn
(C) Ag , Mg and Pb
(D) Al , Cu and Pb

Sol.

ANSWER-KEY**Answer Ex-I****OBJECTIVE PROBLEMS (JEE MAIN)**

1. B	2. B	3. C	4. A	5. B	6. A	7. C
8. D	9. C	10. D	11. C	12. B	13. D	14. C
15. C	16. C	17. B	18. B	19. D	20. A	21. B
22. C	23. C	24. A	25. A	26. A	27. C	28. A
29. B	30. A	31. B	32. C	33. C	34. C	35. B
36. B	37. B	38. B	39. B	40. A	41. B	42. C
43. C	44. B	45. C	46. A	47. A	48. D	49. C
50. B	51. D	52. A	53. B	54. D	55. B	56. B
57. B	58. B	59. B	60. A	61. B	62. A	63. C
64. A	65. A	66. D	67. C	68. A	69. A	70. D

Answer Ex-II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. BCD	2. AB	3. ABCD	4. ACD	5. AB	6. AB	7. AB
8. AB	9. ABC	10. ABC	11. ABC	12. CD	13. BC	14. AC
15. BC	16. AB	17. AC	18. B	19. ABD	20. ABC	21. AC
22. AD	23. AB	24. BC	25. AB	26. AD	27. ABD	28. BD
29. AB	30. AC	31. BC	32. CD	33. ACD	34. BC	35. BC
36. CD	37. A-Q, B-R, C-S, D-P					

Answer Ex-III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. C | 2. A | 3. D | 4. A | 5. C | 6. B | 7. D |
| 8. A | 9. C | 10. D | 11. D | 12. C | 13. D | 14. B |
| 15. B | 16. D | 17. B | 18. A | 19. C | 20. A | 21. B |
| 22. A | 23. C | 24. A | 25. B | 26. A | 27. D | 28. A |
| 29. B | 30. B | | | | | |

Answer Ex-IV**PREVIOUS YEARS PROBLEMS (JEE MAIN)****LEVEL – I****JEE MAIN**

- | | | | | | | |
|------|------|------|------|------|------|------|
| 1. B | 2. D | 3. D | 4. D | 5. C | 6. D | 7. B |
| 8. D | | | | | | |

LEVEL – II**JEE ADVANCED**

- | | | | | | | |
|---------|------|-------|-------|-------|-------|-------|
| 1. C | 2. C | 3. C | 4. B | 5. A | 6. A | 7. A |
| 8. C | 9. B | 10. B | 11. A | 12. D | 13. C | 14. D |
| 15. A,D | | | | | | |

Match the column

25. A-PR, B-P, C-Q, D-S

Q.26 A-P, B-Q, C-PR, D-PS

Fill in the blanks.

27. sitering, smelting

28. B

29. A

d-Block Elements

TRANSITION ELEMENTS

Definition: They are often called "transition elements" because their position in the periodic table is between s-block and p-block elements

Typically, the transition elements have an incompletely filled d-level. Since Zn group has d^{10} configuration and are not considered as transition elements but they are d-block elements.

General Characteristics:

(i) **Metallic character :** They are all metal and good conductor of heat & electricity

(ii) **Electronic configuration :** $(n-1)d^{1-10}ns^{1-2}$

other are as usual {

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			$4s^1$					$4s^1$	
			$3d^5$					$3d^{10}$	

(iii) **M.P.** { Cr, Mo, W } → Maximum 6 no. of unpaired e^- s are involved in metallic bonding

{ Zn, Cd, Hg } → lowest m.p. due to no unpaired e^- for metallic bonding

(iv) **Variation in atomic radius:**

Sc → Mn Fe Co Ni Cu Zn

decreases remains same increases again

(v) **Variable oxidation states possible**

Se	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			+1					+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3		
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

Colour : (aquated)

$Sc^{3+} \rightarrow$ colourless

$Ti^{3+} \rightarrow$ purple

$V^{3+} \rightarrow$ green

$Cr^{2+} \rightarrow$ blue

$Mn^{3+} \rightarrow$ violet

$Fe^{2+} \rightarrow$ light green

$Co^{2+} \rightarrow$ pink

$Cu^{2+} \rightarrow$ blue

Colour : (aquated)

$Ti^{4+} \rightarrow$ colourless

$V^{4+} \rightarrow$ blue

$V^{2+} \rightarrow$ violet

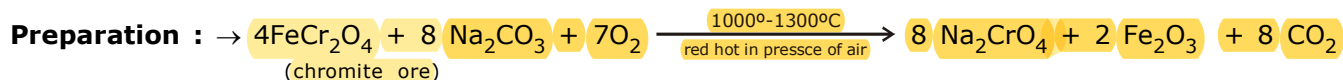
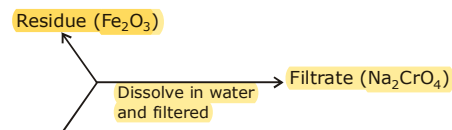
$Cr^{3+} \rightarrow$ green

$Mn^{2+} \rightarrow$ light pink

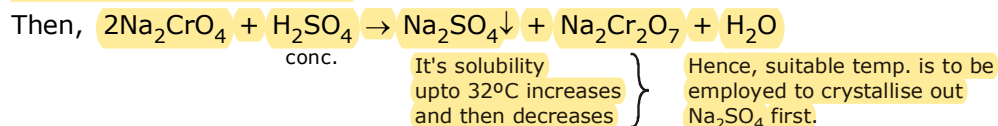
$Fe^{3+} \rightarrow$ yellow

$Ni^{2+} \rightarrow$ green

$Zn^{2+} \rightarrow$ colourless

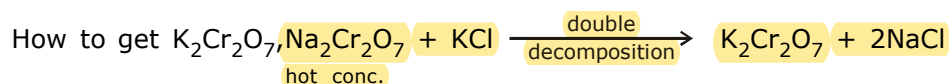
CHROMATE-DICHROMATE

[Lime (CaO) added with Na_2CO_3 which keeps the mass porous so that air has access to all parts and prevents fusion]



Then $\text{Na}_2\text{Cr}_2\text{O}_7$ is crystallised out as $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ on evaporation.

(red crystal)



NaCl crystallises out first and filtered off. Then $\text{K}_2\text{Cr}_2\text{O}_7$ crystallised out on cooling

* Other props & test of CrO_4^{2-} & $\text{Cr}_2\text{O}_7^{2-}$: Already discussed

* Similarities between hexavalent Cr & S-compounds.

- (i) SO_3 & $\text{CrO}_3 \rightarrow$ both acidic.
- (ii) $\text{S} \rightarrow \text{SO}_4^{2-}, \text{S}_2\text{O}_7^{2-}$, $\text{Cr} \rightarrow \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}$
- (iii) CrO_4^{2-} & SO_4^{2-} are isomorphous
- (iv) SO_2Cl_2 & $\text{CrO}_2\text{Cl}_2 \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$ & CrO_4^{2-} respectively
- (v) SO_2Cl^- & $\text{CrO}_3\text{Cl}^- \xrightarrow{\text{OH}^-} \text{SO}_4^{2-}$ & CrO_4^{2-} respectively
- (vi) CrO_3 & $\beta(\text{SO}_3)$ has same structure $\begin{array}{c} \text{O} & \text{O} & \text{O} \\ || & || & || \\ -\text{Cr}- & \text{O}- & \text{Cr}- & \text{O}- & \text{Cr}- \\ || & || & || \\ \text{O} & \text{O} & \text{O} \end{array}$

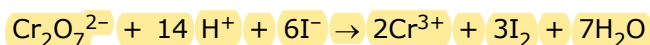
Ques. In laboratory $\text{K}_2\text{Cr}_2\text{O}_7$ is used mainly not $\text{Na}_2\text{Cr}_2\text{O}_7$. Why?

Sol. $\text{Na}_2\text{Cr}_2\text{O}_7$ is deliquescent enough and changes its concentration and can not be taken as primary standard solution whereas $\text{K}_2\text{Cr}_2\text{O}_7$ has no water of crystallisation and not deliquescent.

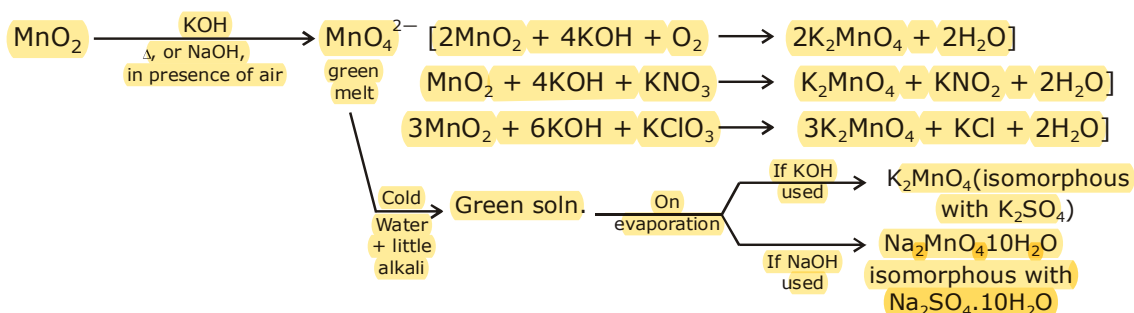
Ques. How to standardise $\text{Na}_2\text{S}_2\text{O}_3$ solution in iodometry?

Sol. $\text{K}_2\text{Cr}_2\text{O}_7$ is primary standard \Rightarrow strength is known by weighing the salt in chemical balance and dissolving in measured amount of water.

Then in acidic solution add. KI

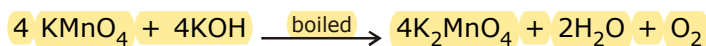


This I_2 is liberated can be estimated with $\text{S}_2\text{O}_3^{2-}$.

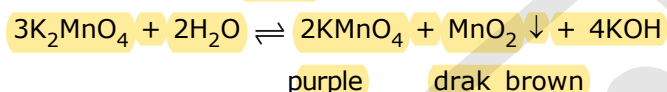
MANGANATE & PERMANGANATEPreparation of Manganate (MnO_4^{2-}):-

In presence of KClO_3 & KNO_3 the above reaction is more faster because these two on decomposition provides O_2 easily.

Manganate is also obtained when KMnO_4 is boiled with KOH .

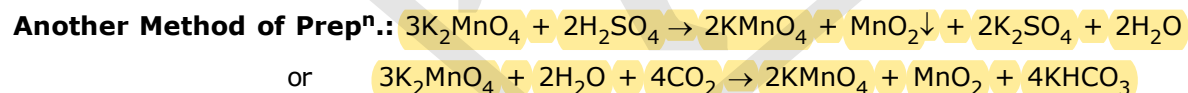


Props : The above green solution is quite stable in alkali, but in pure water and in presence of acids, depositing MnO_2 and giving a purple solution of permanganate.

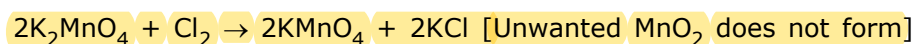


Prob : $E^\circ_{\text{MnO}_4^{2-}/\text{MnO}_2} = 2.26 \text{ V}$ $E^\circ_{\text{MnO}_4^{2-}/\text{MnO}_4^-} = -0.56 \text{ V}$

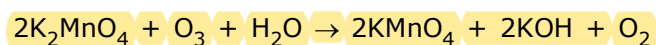
Prove that MnO_4^{2-} will disproportionate in acidic medium.



But in the above method $\frac{1}{3}$ of Mn is lost as MnO_2 but when oxidised either by Cl_2 or by O_3

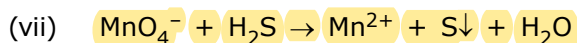
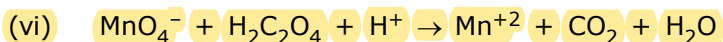
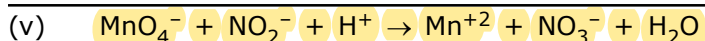


OR



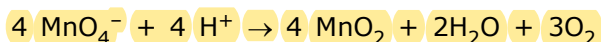
Oxidising Prop. of KMnO_4 : (in acidic medium)

- (i) $\text{MnO}_4^- + \text{Fe}^{+2} + \text{H}^+ \rightarrow \text{Fe}^{+3} + \text{Mn}^{+2} + \text{H}_2\text{O}$
- (ii) $\text{MnO}_4^- + \text{I}^- + \text{H}^+ \rightarrow \text{Mn}^{+2} + \text{I}_2 + \text{H}_2\text{O}$
- (iii) $\text{MnO}_4^- + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Mn}^{+2} + \text{O}_2 + \text{H}_2\text{O}$
- (iv) $\text{MnO}_4^- + \text{SO}_2 \xrightarrow{\text{H}^+} \text{Mn}^{+2} + \text{H}_2\text{SO}_4$



*(1) It is not a primary standard since it is difficult to get it in a high degree of purity and free from traces of MnO_2 .

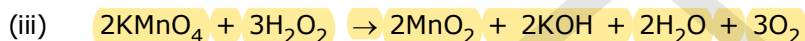
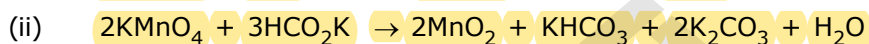
*(2) It is slowly reduced to MnO_2 especially in presence of light or acid



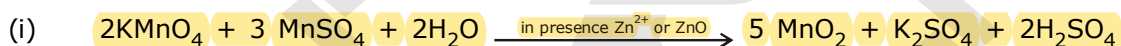
Hence it should be kept in dark bottles and standardise just before use.



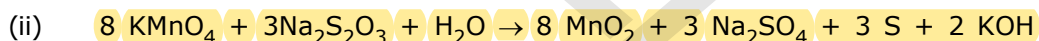
Oxidising Prop. of KMnO_4 in alk. medium :



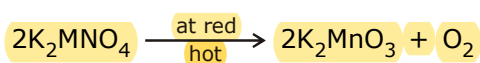
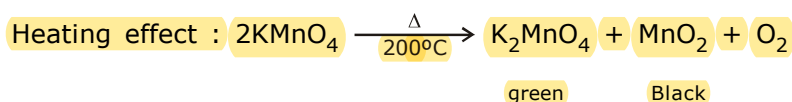
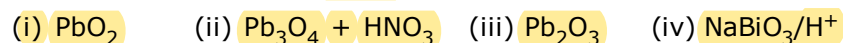
Oxidising Prop. in neutral or weakly acidic solution:

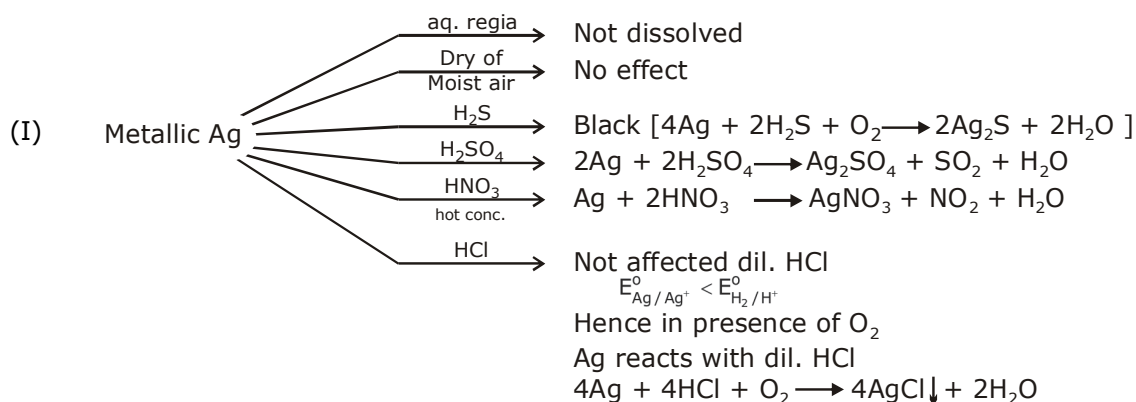


In absence of Zn^{+2} ions, some of the Mn^{+2} ion may escape, oxidation through the formation of insoluble $\text{Mn}^{\text{II}}[\text{Mn}^{\text{IV}}\text{O}_3]$ manganous permanganite.

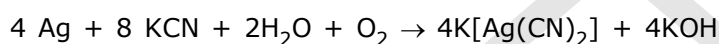


** Conversion of Mn^{+2} to MnO_4^-



SILVER AND ITS COMPOUND

In the same way in presence of O₂, Ag complexes with NaCN/KCN.

**AgNO₃**

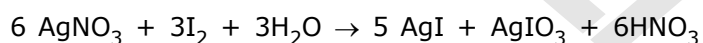
Prepⁿ : Already done.

Properties :

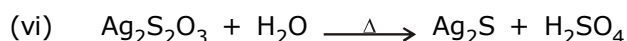
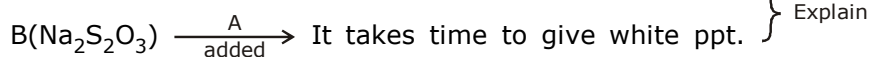
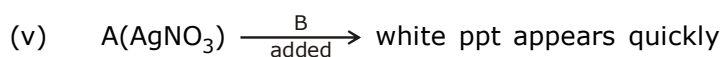
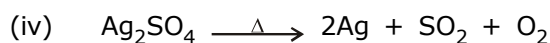
(i) It is called as lunar caustic because in contact with skin it produces burning sensation like that of caustic soda with the formation of finely divided silver (black colour)

(ii) Thermal decomposition:

(iii) Props. of AgNO₃ : [Already done in basic radical]

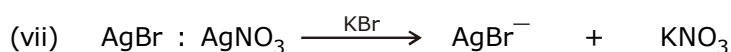


(excess)

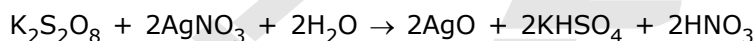
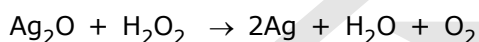
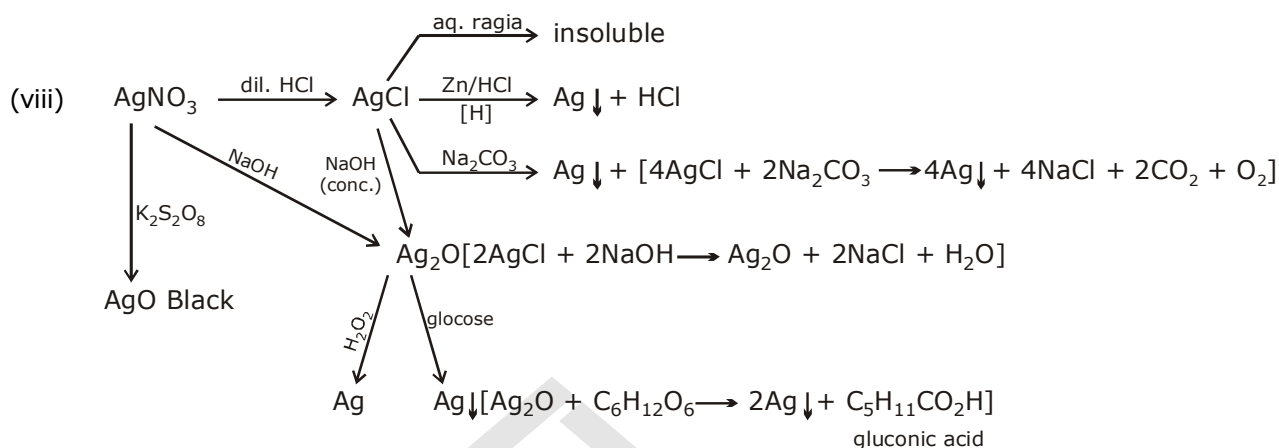
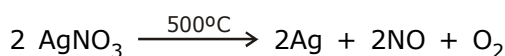
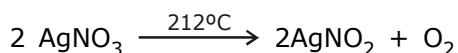


AgCl. AgBr. AgI (but not Ag₂S) are soluble in Na₂S₂O₃ forming

[Ag(S₂O₃)₂]⁻³ complexes



Pale yellow
ppt.

Heating effect :

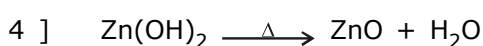
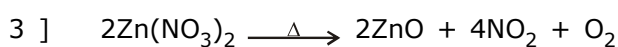
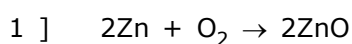
- * AgO supposed to be paramagnetic due to d^9 configuration. But actually it is diamagnetic and exists as

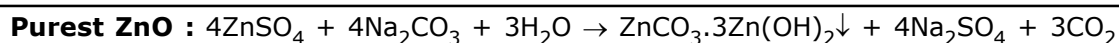


- * Reaction involved in developer:

**ZINC COMPOUNDS**

ZnO : It is called as phillosopher's wool due to its wooly flock type appearance

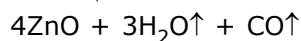
Preparation :



white basic zinc

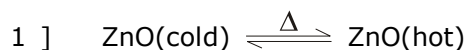
carbonate

Δ



Pure

Properties :



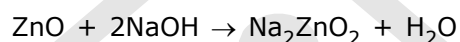
white

yellow

2] It is insoluble in water

3] It sublimes at 400°C

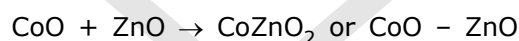
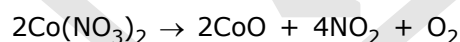
4] It is amphoteric oxide



5] $\text{ZnO} \rightarrow \text{Zn}$ by H_2 & C



6] It forms Rinmann's green with $\text{Co(NO}_3)_2$



Rinmann's green

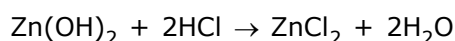
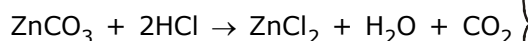
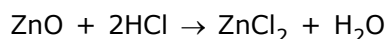
Uses : (1) As white pigment. It is superior than white lead because it does not turn into black

(2) Rinmann's green is used as green pigment

(3) It is used as zinc ointment in medicine

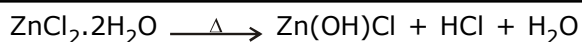
ZnCl₂

Preparation :

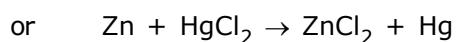
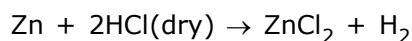


} It crystallises as $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$

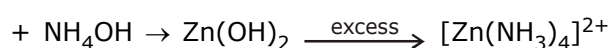
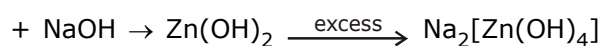
Anh. ZnCl_2 cannot be made by heating $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ because



To get anh. ZnCl_2 : $\text{Zn} + \text{Cl}_2 \rightarrow \text{ZnCl}_2$



Properties : (i) It is deliquescent white solid (when anhydrous)



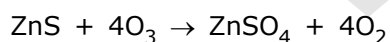
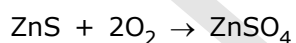
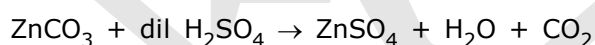
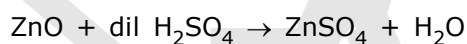
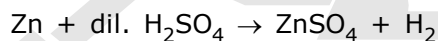
Uses : 1] Used for impregnating timber to prevent destruction by insects

2] As dehydrating agent when anhydrous

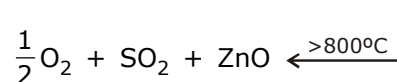
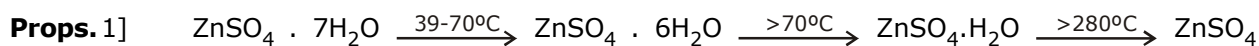
3] ZnO , ZnCl_2 used in dental filling

ZnSO_4 : -

Preparation : \rightarrow

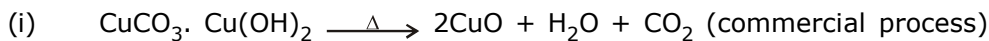


} parallel reaction



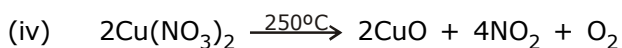
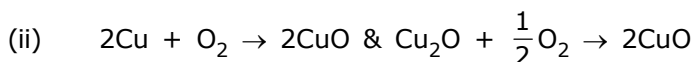
Uses : 1] in eye lotion

2] Lithophone making ($\text{ZnS} + \text{BaSO}_4$) as white pigment.

COPPER COMPOUNDS**CuO :****Preparation : –**

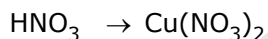
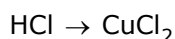
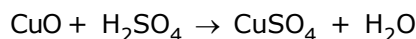
Malachite Green

(native Cu-carbonate)

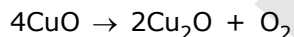
**Properties :**

(i) CuO is insoluble in water

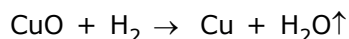
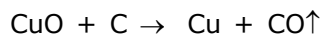
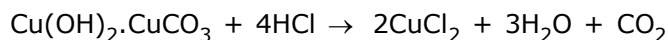
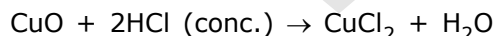
(ii) Readily dissolves in dil. acids



(iii) It decomposes when, heated above 1100°C

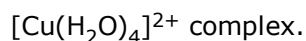


(iv) CuO is reduced to Cu by H_2 or C under hot condition

**CuCl₂ :****Preparation : –****Preparation : –**

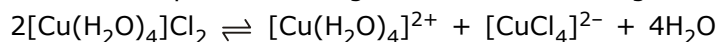
(i) It is crystallised as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ of Emerald green colour

(ii) dil. solution in water is blue in colour due to formation of



(iii) Conc. HCl or KCl added to dil. solution of CuCl_2 the colour changes into yellow, owing to the formation of $[\text{CuCl}_4]^{2-}$.

(iv) The conc. aq. solution is green in colour having the two complex ions in equilibrium



(v) $\text{CuCl}_2 \rightarrow \text{CuCl}$ by no. of reagents

- (a) $\text{CuCl}_2 + \text{Cu-turnings} \xrightarrow{\Delta} 2\text{CuCl}$
 (b) $2\text{CuCl}_2 + \text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{CuCl} + 2\text{HCl} + 2\text{H}_2\text{SO}_4$
 (c) $2\text{CuCl}_2 + \text{Zn/HCl} \rightarrow 2\text{CuCl} + \text{ZnCl}_2$
 (d) $\text{CuCl}_2 + \text{SnCl}_2 \rightarrow \text{CuCl} + \text{SnCl}_4$

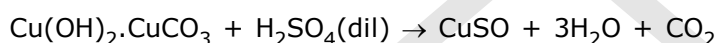
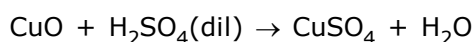
** $\text{CuF}_2 \cdot 2\text{H}_2\text{O} \rightarrow$ light blue
 $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow$ green
 $\text{CuBr}_2 \rightarrow$ almost black

{ Anhyd. CuCl_2 is dark brown mass obtained by heating $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 150°C in presence of HCl vap. }

CuI_2 does not exist $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \xrightarrow[\text{HCl gas}]{150^\circ\text{C}} \text{CuCl}_2 + 2\text{H}_2\text{O}$

CuSO_4 :

Preparation : –



$\text{Cu} + \text{dil. H}_2\text{SO}_4 \rightarrow$ no reaction {Cu is below H in electrochemical series}

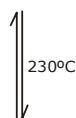
Preparation : –

(i) It is crystallised as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

(ii) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightleftharpoons[\text{efflorescence}]{\text{On exposure}} \text{CuSO}_4 \cdot 3\text{H}_2\text{O} \xrightleftharpoons{100^\circ\text{C}} \text{CuSO}_4 \cdot \text{H}_2\text{O}$

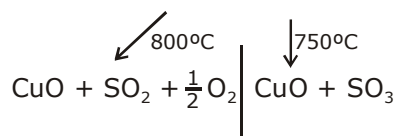
Blue take places Pale blue

Bluish white



$\text{CuSO}_4(\text{anh.})$

white



(iii) Revision with all others reagent

IRON COMPOUNDS**FeSO₄·7H₂O****Preparation : –**

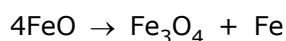
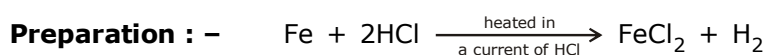
- (i) Scrap Fe + H₂SO₄ → FeSO₄ + H₂↑
(dil.)
- (ii) From Kipp's waste
FeS + H₂SO₄ (dil.) → FeSO₄ + H₂S↑
- (iii) FeS₂ + 2H₂O + $\frac{7}{2}$ O₂ → FeSO₄ + H₂SO₄

Properties : –

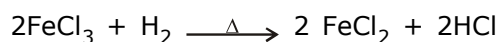
- (i) It undergoes aerial oxidation forming basic ferric sulphate
4FeSO₄ + H₂O + O₂ → 4Fe(OH)SO₄
- (ii) FeSO₄·7H₂O $\xrightarrow{300^\circ\text{C}}$ FeSO₄ $\xrightarrow[\text{temp.}]{\text{high}}$ Fe₂O₃ + SO₂ + SO₃
anh. white
- (iii) Aq. solution is acidic due to hydrolysis
FeSO₄ + 2H₂O ⇌ Fe(OH)₂ + H₂SO₄
weak base
- (iv) It is a reducing agent
- (a) Fe²⁺ + MnO₄⁻ + H⁺ → Fe³⁺ + Mn²⁺ + H₂O
- (b) Fe²⁺ + Cr₂O₇²⁻ + H⁺ → Fe³⁺ + Cr³⁺ + H₂O
- (c) Au³⁺ + Fe²⁺ → Au + Fe³⁺
- (d) Fe²⁺ + HgCl₂ → Hg₂Cl₂↓ + Fe³⁺
white ppt.
- (v) It forms double salt. Example (NH₄)₂SO₄·FeSO₄·6H₂O

FeO(Black) :

Props : – It is stable at high temperature and on cooling slowly disproportionates into Fe_3O_4 and iron.

**FeCl₂ :**

OR

**Properties: –**

- (i) It is deliquescent in air like FeCl_3
- (ii) It is soluble in water, alcohol and ether also because it is sufficiently covalent in nature.
- (iii) It volatilises at about 1000°C and vapour density indicates the presence of Fe_2Cl_4 . Above 1300°C density becomes normal
- (iv) It oxidises on heating in air
$$12\text{FeCl}_2 + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 8\text{FeCl}_3$$
- (v) H_2 evolves on heating in steam
$$3\text{FeCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{HCl} + \text{H}_2$$
- (vi) It can exist as different hydrated form
$$\text{FeCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Colourless}$$
$$\text{FeCl}_2 \cdot 4\text{H}_2\text{O} \rightarrow \text{pale green}$$
$$\text{FeCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{green}$$

EXERCISE – I

OBJECTIVE PROBLEMS (JEE MAIN)

1. (T) imparts violet colour $\xrightarrow{\text{compd(U)} + \text{conc. H}_2\text{SO}_4}$ (V)

Red gas $\xrightarrow{\text{NaOH} + \text{AgNO}_3}$ (W) Red ppt.

$\xrightarrow{\text{NH}_3 \text{ soln.}}$ (X)

(W) Red ppt. $\xrightarrow{\text{dil. HCl}}$ (Y) white ppt.

(U) $\xrightarrow[\Delta]{\text{NaOH}}$ (Z) gas (gives white fumes with HCl) sublimes on heating

Identify (T) to (Z).

(A) T = KMnO_4 , U = HCl, V = Cl_2 , W = HgI_2 , X = $\text{Hg}(\text{NH}_2)\text{NO}_3$, Y = Hg_2Cl_2 , Z = N_2

(B) T = $\text{K}_2\text{Cr}_2\text{O}_7$, U = NH_4Cl , V = CrO_2Cl_2 , W = Ag_2CrO_4 , X = $[\text{Ag}(\text{NH}_3)_2]^+$, Y = AgCl, Z = NH_3

(C) T = K_2CrO_4 , U = KCl, V = CrO_2Cl_2 , W = HgI_2 , X = Na_2CrO_4 , Y = BaCO_3 , Z = NH_4Cl

(D) T = K_2MnO_4 , U = NaCl, V = CrO_3 , W = AgNO_2 , X = $(\text{NH}_4)_2\text{CrO}_4$, Y = CaCO_3 , Z = SO_2

Sol.

2. The number of moles of acidified KMnO_4 required to convert one mole of sulphite ion into sulphate ion is-

(A) 2/5 (B) 3/5 (C) 4/5 (D) 1

Sol.

3. $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{\text{Fe} + \text{Mo}} 2\text{NH}_3(\text{g})$; Haber's process, Mo is used as -

(A) a catalyst (B) a catalytic promoter
(C) an oxidising agent (D) as a catalytic poison

Sol.

4. Potash alum is a double salt, its aqueous solution shows the characteristics of-

(A) Al^{3+} ions (B) K^+ ions
(C) SO_4^{2-} ions
(D) Al^{3+} ions but not K^+ ions

Sol.

5. $\text{Cr}_2\text{O}_7^{2-} \xrightleftharpoons[X]{Y} 2\text{CrO}_4^{2-}$, X and Y are respectively-

(A) X = OH^- , Y = H^+ (B) X = H^+ , Y = OH^-
(C) X = OH^- , Y = H_2O_2 (D) X = H_2O_2 , Y = OH^-

Sol.

6. Addition of non-metals like B and C to the interstitial sites of a transition metal results the metal-

(A) of more ductability (B) of less ductability
(C) less malleable (D) of more hardness

Sol.

7. Mercury is a liquid at 0°C because of-

(A) very high ionisation energy
(B) weak metallic bonds
(C) high heat of hydration
(D) high heat of sublimation

Sol.

8. CrO_3 dissolves in aqueous NaOH to give-

(A) $\text{Cr}_2\text{O}_7^{2-}$ (B) CrO_4^{2-}
(C) $\text{Cr}(\text{OH})_3$ (D) $\text{Cr}(\text{OH})_2$

Sol.

9. The correct statement(s) about transition elements is/are-

(A) the most stable oxidation state is +3 and its stability decreases across the period
(B) transition elements of 3d- series have almost same atomic sizes from Cr to Cu
(C) the stability of +2 oxidation state increases across the period.
(D) some transition elements like Ni, Fe, Cr may show zero oxidation state in some of their compounds

Sol.

- 10.** An ornament of gold having 75% of gold, it is of carat.

(A) 18 (B) 16
(C) 24 (D) 20

Sol.

- 11.** Solution of MnO_4^- is purple-coloured due to-
(A) d-d- transition
(B) charge transfer from O to Mn
(C) due to both d-d-transition and charge transfer
(D) none of these

Sol.

- 12.** The ionisation energies of transition elements are-
(A) less than p-block elements
(B) more than s-block elements
(C) less than s-block elements
(D) more than p-block elements

Sol.

- 13.** Transition elements having more tendency to form complex than representative elements (s and p-block elements) due to-
(A) availability of d-orbitals for bonding
(B) variable oxidation states are not shown by transition elements
(C) all electrons are paired in d-orbitals
(D) f-orbitals are available for bonding

Sol.

- 14.** During estimation of oxalic acid Vs KMnO_4 , self indicator is-
(A) KMnO_4 (B) oxalic acid
(C) K_2SO_4 (D) MnSO_4

Sol.

- 15.** The metal(s) which does/do not form amalgam is/are-
(A) Fe (B) Pt (C) Zn (D) Ag

Sol.

- 16.** Which of the following statements concern with transition metals ?
(A) compounds containing ions of transition elements are usually coloured
(B) the most common oxidation state is +3
(C) they show variable oxidation states, which differ by two units only
(D) they easily form complexes

Sol.

- 17.** Correct statement(s) is/are-
(A) an acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$ liberates iodine from KI
(B) $\text{K}_2\text{Cr}_2\text{O}_7$ is used as a standard solution for estimation of Fe^{2+} ions
(C) in acidic medium, $M = N/6$ for $\text{K}_2\text{Cr}_2\text{O}_7$
(D) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ on heating decomposes to yield Cr_2O_3 through an endothermic reaction

Sol.

- 18.** The highest oxidation state among transition elements is-
(A) + 7 by Mn (B) + 8 by Os
(C) +8 by Ru (D) +7 by Fe

Sol.

- 19.** A compound of mercury used in cosmetics, in Ayurvedic and Yunani medicines and known as Vermilion is-
(A) HgCl_2 (B) HgS (C) Hg_2Cl_2 (D) HgI

Sol.

20. Acidified chromic acid + $\text{H}_2\text{O}_2 \xrightarrow[\text{(blue colour)}]{\text{Org. solvent}} \text{X} + \text{Y}$,
X and Y are –
(A) CrO_5 and H_2O (B) Cr_2O_3 and H_2O
(C) CrO_2 and H_2O (D) CrO and H_2O

Sol.

21. $\uparrow \text{Y(g)} \xleftarrow{\text{KI}} \text{CuSO}_4 \xrightarrow{\text{dil H}_2\text{SO}_4} \text{X (Blue colour)}$, X and Y are –
(A) $\text{X} = \text{I}_2$, $\text{Y} = [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$
(B) $\text{X} = [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$, $\text{Y} = \text{I}_2$
(C) $\text{X} = [\text{Cu}(\text{H}_2\text{O})_4]^+$, $\text{Y} = \text{I}_2$
(D) $\text{X} = [\text{Cu}(\text{H}_2\text{O})_5]^{2+}$, $\text{Y} = \text{I}_2$

Sol.

22. Transition elements are usually characterised by variable oxidation states but Zn does not show this property because of –
(A) completion of np-orbitals
(B) completion of (n–1) d orbitals
(C) completion of ns-orbitals
(D) inert pair effect

Sol.

23. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (Ammonium dichromate) is used in fire works. The green coloured powder blown in air is –
(A) Cr_2O_3 (B) CrO_2 (C) Cr_2O_4 (D) CrO_3

Sol.

24. The d-block element which is a liquid at room temperature, having high specific heat, less reactivity than hydrogen and its chloride (MX_2) is volatile on heating is –
(A) Cu (B) Hg (C) Ce (D) Pm

Sol.

25. Coinage metals show the properties of –
(A) typical elements
(B) normal elements
(C) inner-transition elements
(D) transition element

Sol.

26. Iron becomes passive by.....due to formation of
(A) dil. HCl, Fe_2O_3
(B) 80% conc. HNO_3 , Fe_3O_4
(C) conc. H_2SO_4 , Fe_3O_4
(D) conc. HCl, Fe_3O_4

Sol.

27. Bayer's reagent used to detect olifinic double bond is –
(A) acidified KMnO_4
(B) aqueous KMnO_4
(C) 1% alkaline KMnO_4 solution
(D) KMnO_4 in benzene

Sol.

28. Amphoteric oxide(s) is/are –
(A) Al_2O_3 (B) SnO (C) ZnO (D) Fe_2O_3

Sol.

29. Interstitial compounds are formed by –
(A) Co (B) Ni (C) Fe (D) Ca

Sol.

30. The transition metal used in X-rays tube is –
(A) Mo (B) Ta (C) Tc (D) Pm

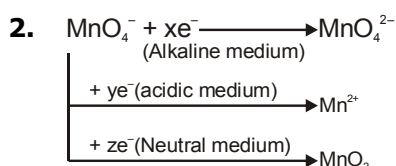
Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. The catalytic activity of transition elements is related to their-

(A) variable oxidation states
(B) surface area
(C) complex formation ability
(D) magnetic moment

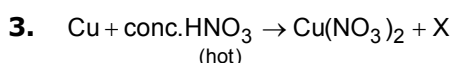
Sol.



x, y and z are respectively-

(A) 1, 2, 3 (B) 1, 5, 3 (C) 1, 3, 5 (D) 5, 3, 1

Sol.



(oxide of nitrogen) ; then X is-

(A) N_2O (B) NO_2 (C) NO (D) N_2O_3

Sol.

4. When KMnO_4 solution is added to hot oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time. This is because-

(A) Mn^{2+} acts as auto catalyst
(B) CO_2 is formed
(C) Reaction is exothermic
(D) MnO_4^- catalyses the reaction.

Sol.

5. CuSO_4 solution reacts with excess KCN to give -

(A) Cu(CN)_2 (B) CuCN
(C) $\text{K}_2[\text{Cu(CN)}_2]$ (D) $\text{K}_3[\text{Cu(CN)}_4]$

Sol.

6. The higher oxidation states of transition elements are found to be in the combination A and B, which are -

(A) F, O (B) O, N (C) O, Cl (D) F, Cl

Sol.

7. In the equation $\text{M} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4[\text{M(CN)}_2]^- + 4\text{OH}^-$, metal M is-

(A) Ag (B) Au (C) Cu (D) Hg

Sol.

8. An element of 3d-transition series shows two oxidation states x and y , differ by two units then

- (A) compounds in oxidation state x are ionic if $x > y$
(B) compounds in oxidation state x are ionic if $x < y$
(C) compound in oxidation state y are covalent if $x < y$
(D) compounds in oxidation state y are covalent if $y < x$

Sol.

9. Pick out the incorrect statement :

- (A) MnO_2 dissolves in conc. HCl , but does not form Mn^{4+} ions
(B) MnO_2 oxidizes hot concentrated H_2SO_4 liberating oxygen
(C) K_2MnO_4 is formed when MnO_2 in fused KOH is oxidised by air, KNO_3 , PbO_2 or NaBiO_3
(D) Decomposition of acidic KMnO_4 is not catalysed by sunlight.

Sol.

10. 1 mole of Fe^{2+} ions are oxidised to Fe^{3+} ions with the help of (in acidic medium)

- (A) $1/5$ moles of KMnO_4 (B) $5/3$ moles of KMnO_4
(C) $2/5$ moles of KMnO_4 (D) $5/2$ moles of KMnO_4

Sol.

11. The metals present in insulin and haemoglobin are respectively-

- (A) Zn, Hg (B) Zn, Fe (C) Co, Fe (D) Mg, Fe

Sol.

12. To an acidified dichromate solution, a pinch of Na_2O_2 is added and shaken. What is observed.

- (A) blue colour
(B) Orange colour changing to green
(C) Copious evolution of oxygen
(D) Bluish-green precipitate

Sol.

13. The rusting of iron is formulated as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ which involves the formation of -

- (A) Fe_2O_3 (B) $\text{Fe}(\text{OH})_3$
(C) $\text{Fe}(\text{OH})_2$ (D) $\text{Fe}_2\text{O}_3 + \text{Fe}(\text{OH})_3$

Sol.

14. Metre scales are made-up-of alloy

- (A) invar (B) stainless steel
(C) elektron (D) magnalium

Sol.

15. Amongst CuF_2 , CuCl_2 and CuBr_2

- (A) only CuF_2 is ionic
(B) both CuCl_2 and CuBr_2 are covalent
(C) CuF_2 and CuCl_2 are ionic but CuBr_2 is covalent
(D) CuF_2 , CuCl_2 as well as CuBr_2 are ionic

Sol.

16. A metal M which is not affected by strong acids like conc. HNO_3 , conc. H_2SO_4 and conc. solution of alkalies like NaOH , KOH forms MCl_3 which finds use for toning in photography. The metal M is-
- (A) Ag (B) Hg (C) Au (D) Cu

Sol.

17. Solid $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ having covalent, ionic as well as co-ordinate bonds. Copper atom/ion forms.....co-ordinate bonds with water.
- (A) 1 (B) 2 (C) 3 (D) 4

Sol.

18. $\text{CuSO}_4(\text{aq}) + 4\text{NH}_3 \rightarrow \text{X}$, then X is-
- (A) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ (B) paramagnetic
(C) coloured
(D) of a magnetic moment of 1.73 BM

Sol.

19. $\text{KMnO}_4 + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{X}(\text{g})$, X is a (acidified)
- (A) red liquid (B) violet gas
(C) greenish yellow gas (D) yellow-brown gas

Sol.

20. Purple of cassius is :
(A) Pure gold
(B) Colloidal solution of gold
(C) Gold (I) hydroxide
(D) Gold (III) chloride

Sol.

21. Amongst the following species, maximum covalent character is exhibited by-
- (A) FeCl_2 (B) ZnCl_2 (C) HgCl_2 (D) CdCl_2

Sol.

22. Number of moles of SnCl_2 required for the reduction of 1 mole of $\text{K}_2\text{Cr}_2\text{O}_7$ into Cr_2O_3 is (in acidic medium)
- (A) 3 (B) 2 (C) 1 (D) $1/3$

Sol.

23. Amphoteric oxide(s) of Mn is/are-
- (A) MnO_2 (B) Mn_3O_4 (C) Mn_2O_7 (D) MnO

Sol.

24. Pick out the incorrect statement :
(A) MnO_4^{2-} is quite strongly oxidizing and stable only in very strong alkalies. In dilute alkali, neutral solutions, it disproportionates.

(B) In acidic solutions, MnO_4^- is reduced to Mn^{2+} and thus, KMnO_4 is widely used as oxidising agent
(C) KMnO_4 does not act as oxidising agent in alkaline medium
(D) KMnO_4 is manufactured by the fusion of pyrolusite ore with KOH in presence of air or KNO_3 , followed by electrolytic oxidation in alkaline solution.

Sol.

25. The aqueous solution of CuCrO_4 is green because it contains-

- (A) green Cu^{2+} ions
- (B) green CrO_4^{2-} ions
- (C) blue Cu^{2+} ions and green CrO_4^{2-} ions
- (D) blue Cu^{2+} ions and yellow CrO_4^{2-} ions

Sol.

26. Manganese steel is used for making railway tracks because-

- (A) it is hard with high percentage of Mn
- (B) it is soft with high percentage of Mn
- (C) it is hard with small concentration of manganese with impurities
- (D) it is soft with small concentration of manganese with impurities

Sol.

27. In nitroprusside ion, the iron exists as Fe^{2+} and NO as NO^+ rather than Fe^{3+} and NO respectively. These forms of ions are established with the help of-

- (A) magnetic moment in solid state
- (B) thermal decomposition method
- (C) by reaction with KCN
- (D) by action with K_2SO_4

Sol.

28. Acidified KMnO_4 can be decolourised by-

- (A) SO_2
- (B) H_2O_2
- (C) FeSO_4
- (D) $\text{Fe}_2(\text{SO}_4)_3$

Sol.

29. Transition elements in lower oxidation states act as Lewis acid because-

- (A) they form complexes
- (B) they are oxidising agents
- (C) they donate electrons
- (D) they do not show catalytic properties

Sol.

30. The lanthanide contraction is responsible for the fact that-

- (A) Zr and Hf have same atomic sizes
- (B) Zr and Hf have same properties
- (C) Zr and Hf have different atomic sizes
- (D) Zr and Hf have different properties

Sol.

EXERCISE – III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. The Ziegler-Natta catalyst used for polymerisation of ethene and styrene is $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al}$, the catalysing species (active species) involved in the polymerisation is-

(A) TiCl_4 (B) TiCl_3 (C) TiCl_2 (D) TiCl

Sol.

2. Ion(s) having non zero magnetic moment (spin only) is/are-

(A) Sc^{3+} (B) Ti^{3+} (C) Cu^{2+} (D) Zn^{2+}

Sol.

3. The electrons which take part in order to exhibit variable oxidation states by transition metals are
(A) ns only (B) $(n-1)d$ only
(C) ns and $(n-1)d$ only but not up
(D) $\text{CuO} + \text{CaO}$

Sol.

4. 'Bordeaux mixture' is used as a fungicide. It is a mixture of-

(A) $\text{CaSO}_4 + \text{Cu}(\text{OH})_2$ (B) $\text{CuSO}_4 + \text{Ca}(\text{OH})_2$
(C) $\text{CuSO}_4 + \text{CaO}$ (D) $\text{CuO} + \text{CaO}$

Sol.

5. Which of the following reaction is possible at anode ?

(A) $2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$
(B) $\text{F}_2 + 2\text{F}^-$
(C) $\frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}$ (D) None of these

Sol.

6. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue ?

(A) KNO_3 (B) AgNO_3 (C) $\text{Zn}(\text{NO}_3)_2$ (D) ZnSO_4

Sol.

7. Peacock ore is -

(A) FeS_2 (B) CuFeS_2
(C) $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (D) Cu_5FeS_4

Sol.

8. "925 fine silver" means an alloy of :

(A) 7.5% Ag and 92.5% Cu
(B) 92.5% Ag and 7.5% Cu
(C) 80% Ag and 20% Cu
(D) 90% Ag and 10% Cu

Sol.

9. Iron salt used in blue prints is :

(A) FeC_2O_4 (B) $\text{Fe}_2(\text{C}_2\text{O}_4)_3$
(C) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (D) $\text{K}_3[\text{Fe}(\text{CN})_6]$

Sol.

10. When acidified KMnO_4 is added to hot oxalic acid solution, the decolourization is slow in the beginning, but becomes very rapid after some time. This is because :

- (A) Mn^{2+} acts as autocatalyst
- (B) CO_2 is formed as the product
- (C) Reaction is exothermic
- (D) MnO_4^- catalyses the reaction

Sol.

Sol.

14. Assertion : CrO_3 reacts with HCl to form chromyl chloride gas.

Reason : Chromyl chloride (CrO_2Cl_2) has tetrahedral shape.

Sol.

15. Assertion : Zinc does not show characteristic properties of transition metals.

Reason : In zinc outermost shell is completely filled.

Sol.

16. Assertion : Tungsten has a very high melting point.

Reason : Tungsten is a covalent compound.

Sol.

17. Assertion : Equivalent mass of KMnO_4 is equal to one-third of its molecular mass when it acts as an oxidising agent in an alkaline medium.

Reason : Oxidation number of Mn is +7 in KMnO_4 .

Sol.

12. Assertion : K_2CrO_4 has yellow colour due to charge transfer.

Reason : CrO_4^{2-} ion is tetrahedral in shape.

Sol.

18. Assertion : Ce^{4+} is used as an oxidising agent in volumetric analysis.

Reason : Ce^{4+} has the tendency to attain +3 oxidation state.

Sol.

13. Assertion : The highest oxidation state of chromium in its compounds is +6.

Reason : Chromium atom has only six electrons in ns and (n-1)d orbitals.

19. Assertion : Promethium is a man made element.

Reason : It is radioactive and has been prepared by artificial means.

Sol.

20. Assertion : Cu^+ ion is colourless.

Reason : Four water molecules are coordinated to Cu^+ ion.

Sol.

21. Among d-block elements, the most abundant element belongs to the :

- (A) first transition series
- (B) second transition series
- (C) third transition series
- (D) fourth transition series

Sol.

22. The 3d metal ions are generally paramagnetic in nature because :

- (A) they form coloured salts
- (B) they have one or more unpaired d electrons
- (C) they have one or more paired s electrons
- (D) they are reducing agents

Sol.

23. Green vitriol is formed by :

- (A) $\text{FeS}_2 + \text{CO}$
- (B) $\text{FeS}_2 + \text{H}_2\text{O} + \text{CO}_2$
- (C) $\text{FeS}_2 + \text{H}_2\text{O} + \text{O}_2$
- (D) $\text{FeS}_2 + \text{CO} + \text{CO}_2$

Sol.

24. Which of the following forms with an excess of CN^- , a complex having coordination number two ?

- (A) Cu^{2+}
- (B) Ag^+
- (C) Ni^{2+}
- (D) Fe^{2+}

Sol.

25. Of the following outer electronic configurations of atoms, the highest oxidation state is achieved by which one of them ?

- (A) $(n-1)d^8ns^2$
- (B) $(n-1)d^5ns^1$
- (C) $(n-1)d^3ns^2$
- (D) $(n-1)d^5ns^2$

Sol.

26. In which of the following pairs are both the ions coloured in aqueous solution ?

- (A) Sc^{3+} , Co^{2+}
- (B) Ni^{2+} , Cu^+
- (C) Ni^{2+} , Ti^{3+}
- (D) Sc^{3+} , Ti^{3+}

Sol.

27. Which of the following has the maximum number of unpaired d electrons ?

- (A) Zn
- (B) Fe^{2+}
- (C) Ni^{3+}
- (D) Cu^+

Sol.

28. Colour in transition metal compounds is attributed to :

- (A) small size of metal ions
- (B) absorption of light in UV region
- (C) moderate ionisation energy
- (D) incomplete $(n-1)d$ subshell

Sol.

29. The property, which is not characteristic of transition metals, is :

- (A) variable oxidation states
- (B) tendency to form complexes
- (C) formation of coloured compounds
- (D) natural radioactivity

Sol.

30. The correct order of ionisation energy is :

- (A) $\text{Cu} > \text{Ag} > \text{Au}$
- (B) $\text{Cu} > \text{Au} > \text{Ag}$
- (C) $\text{Au} > \text{Cu} > \text{Ag}$
- (D) $\text{Ag} > \text{Au} > \text{Cu}$

Sol.

EXERCISE – IV

PREVIOUS YEARS

LEVEL – I

JEE MAIN

Q.1 Arrange Ce^{3+} , La^{3+} , Pm^{3+} , and Yb^{3+} in increasing order of their ionic radius –

[AIEEE-02]

- (A) $\text{Yb}^{3+} < \text{Pm}^{3+} < \text{Ce}^{3+} < \text{La}^{3+}$
 (B) $\text{Ce}^{3+} > \text{Yb}^{3+} < \text{Pm}^{3+} < \text{La}^{3+}$
 (C) $\text{Yb}^{3+} > \text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+}$
 (D) $\text{Pm}^{3+} < \text{La}^{3+} < \text{Ce}^{3+} < \text{Yb}^{3+}$

Sol.

Q.2 What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid –

[AIEEE-03]

- (A) Cr^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ are formed
 (B) $\text{Cr}_2\text{O}_7^{2-}$ and H_2O are formed
 (C) $\text{Cr}_2\text{O}_7^{2-}$ is reduced to +3 state of Cr
 (D) $\text{Cr}_2\text{O}_7^{2-}$ is oxidised to +7 state of Cr

Sol.

Q.3 The radius of La^{3+} is 1.06 \AA , which of the following given values will be closest to the radius of Lu^{3+} (At no. of Lu = 71, La = 57) –

[AIEEE-03]

- (A) 1.6 \AA (B) 1.4 \AA
 (C) 1.06 \AA (D) 0.85 \AA

Sol.

Q.4 Cerium ($Z = 58$) is an important member of the lanthanoids. Which of the following statement about cerium is incorrect –

[AIEEE-04]

- (A) Cerium (IV) acts as an oxidising agent
 (B) The +3 oxidation state of cerium is more stable than the +4 oxidation state
 (C) The +4 oxidation state of cerium is not known in solutions
 (D) The common oxidation states of cerium are +3 and +4

Sol.

Q.5 Excess of KI reacts with CuSO_4 solution and then $\text{Na}_2\text{S}_2\text{O}_3$ solution is added to it. Which of the statements is incorrect for this reaction –

[AIEEE-04]

- (A) Evolved I_2 is reduced
 (B) CuI_2 is formed
 (C) $\text{Na}_2\text{S}_2\text{O}_3$ is oxidised
 (D) Cu_2I_2 is formed

Sol.

Q.6 Calomel on reaction with NH_4OH gives –

[AIEEE-04]

- (A) HgNH_2Cl (B) $\text{NH}_2\text{--Hg--Hg--Cl}$
 (C) Hg_2O (D) HgO

Sol.

Q.7 The lanthanoid contraction is responsible for the fact that –

[AIEEE-05]

- (A) Zr and Y have about the same radius
 (B) Zr and Nb have similar oxidation state
 (C) Zr and Hf have about the same radius
 (D) Zr and Zn have similar oxidation state

Sol.

Q.8 Lanthanoid contraction is caused due to –

[AIEEE-06]

- (A) the same effective nuclear charge from Ce to Lu
 (B) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge
 (C) the appreciable shielding on outer electrons by 4f electrons from the nuclear charge
 (D) the appreciable shielding on outer electrons by 5d electrons from the nuclear charge

Sol.

Q.9 Identify the incorrect statement among the following - **[AIEEE-07]**

- (A) d-block elements show irregular and erratic chemical properties among themselves
- (B) La and Lu have partially filled d-orbitals and no other partially filled orbitals
- (C) The chemistry of various lanthanoids is very similar
- (D) 4f and 5f-orbitals are equally shielded

Sol.

Q.10 The actinoids exhibits more number of oxidation states in general than the lanthanoids. This is because - **[AIEEE-07]**

- (A) The 5f-orbitals are more buried than the 4f-orbitals
- (B) There is a similarity between 4f-and-5f in their angular part of the wave function
- (C) The actinoids are more reactive than the lanthanoids
- (D) The 5f-orbitals extend further from the nucleus than the 4f-orbitals

Sol.

Q.11 In context with the transition elements, which of the following statements is incorrect ? **[AIEEE-09]**

- (A) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
- (B) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and electrons are used for bonding.
- (C) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
- (D) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

Sol.

Q.12 Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statements is incorrect ? **[AIEEE-09]**

- (A) The ionic sizes of Ln (III) decrease in general with increasing atomic number.
- (B) Ln (III) compounds are generally colourless.
- (C) Ln (III) hydroxides are mainly basic in character.
- (D) Because of the large size of the Ln (III) ions the bonding in its compounds is predominantly ionic in character.

Sol.

Q.13 Iron exhibits + 2 and + 3 oxidation states. Which of the following statements about iron is incorrect ? **[AIEEE-2012]**

- (A) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
- (B) Ferrous compounds are less volatile than the corresponding ferric compounds
- (C) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds
- (D) Ferrous oxide is more basic in nature than the ferric oxide

Sol.

LEVEL – II

JEE ADVANCED

Q.1 Which of the following statement (s) is (are) correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ?

[IIT-1998]

- (A) A deep red vapour is evolved
(B) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4
(C) Chlorine gas is evolved
(D) Chromyl chloride is formed

Sol.

Q.2 In the dichromate dianion, [IIT-1999]

- (A) 4, Cr-O bonds are equivalent
(B) 6, Cr-O bonds are equivalent
(C) All, Cr-O bonds are equivalent
(D) All, Cr-O bonds are non-equivalent

Sol.

Q.3 Which of the following compounds exhibit the same colour in the aqueous solution ?

[IIT-2007]

- (A) $VOCl_2$ & $FeCl_2$ (B) $FeCl_2$ & $CuCl_2$
(C) $MnCl_2$ & $FeCl_2$ (D) $VOCl_2$ & $CuCl_2$

Sol.

Q.4 Reduction of the metal centre in aqueous permanganate ion involves [IIT-2011]

- (A) 3 electrons in neutral medium
(B) 5 electrons in neutral medium
(C) 3 electrons in alkaline medium
(D) 5 electrons in acidic medium

Sol.

Q.5 The colour of light absorbed by an aqueous solution of $CuSO_4$ is - [IIT-2012]

- (A) orange-red (B) blue-green
(C) yellow (D) violet

Sol.

Q.6 Which of the following hydrogen halides react(s) with $AgNO_3(aq)$ to give a precipitate that dissolves in $Na_2S_2O_3(aq)$? [IIT-2012]

- (A) HCl (B) HF
(C) HBr (D) HI

Sol.

Answers

Exercise-I

1. B	2. A	3. B	4. ABC	5. A
6. BCD	7. AB	8. B	9. ABCD	10. A
11. B	12. AB	13. A	14. A	15. AB
16. ABD	17. ABC	18. BC	19. B	20. A
21. B	22. B	23. A	24. B	25. D
26. B	27. C	28. ABC	29. ABC	30. A

Exercise-II

1. ABC	2. B	3. B	4. A	5. D
6. A	7. AB	8. BC	9. D	10. A
11. B	12. AC	13. D	14. A	15. AB
16. C	17. D	18. ABCD	19. C	20. B
21. C	22. A	23. AB	24. C	25. D
26. A	27. A	28. ABC	29. C	30. AB

Exercise-III

1. B	2. BC	3. C	4. B	5. A
6. B	7. D	8. B	9. B	10. A
11. B	12. B	13. A	14. B	15. C
16. C	17. B	18. A	19. A	20. C
21. A	22. B	23. C	24. B	25. D
26. C	27. B	28. D	29. D	30. C

Exercise-IV

Level-I

Ques.	1	2	3	4	5	6	7	8	9	10	11	12	13
Ans.	A	B	D	C	B	A	C	B	D	D	A	B	C

Level-II

Ques.	1	2	3	4	5	6
Ans.	A,B,D	B	D	A,C,D	A	A, C, D

SALT ANALYSIS

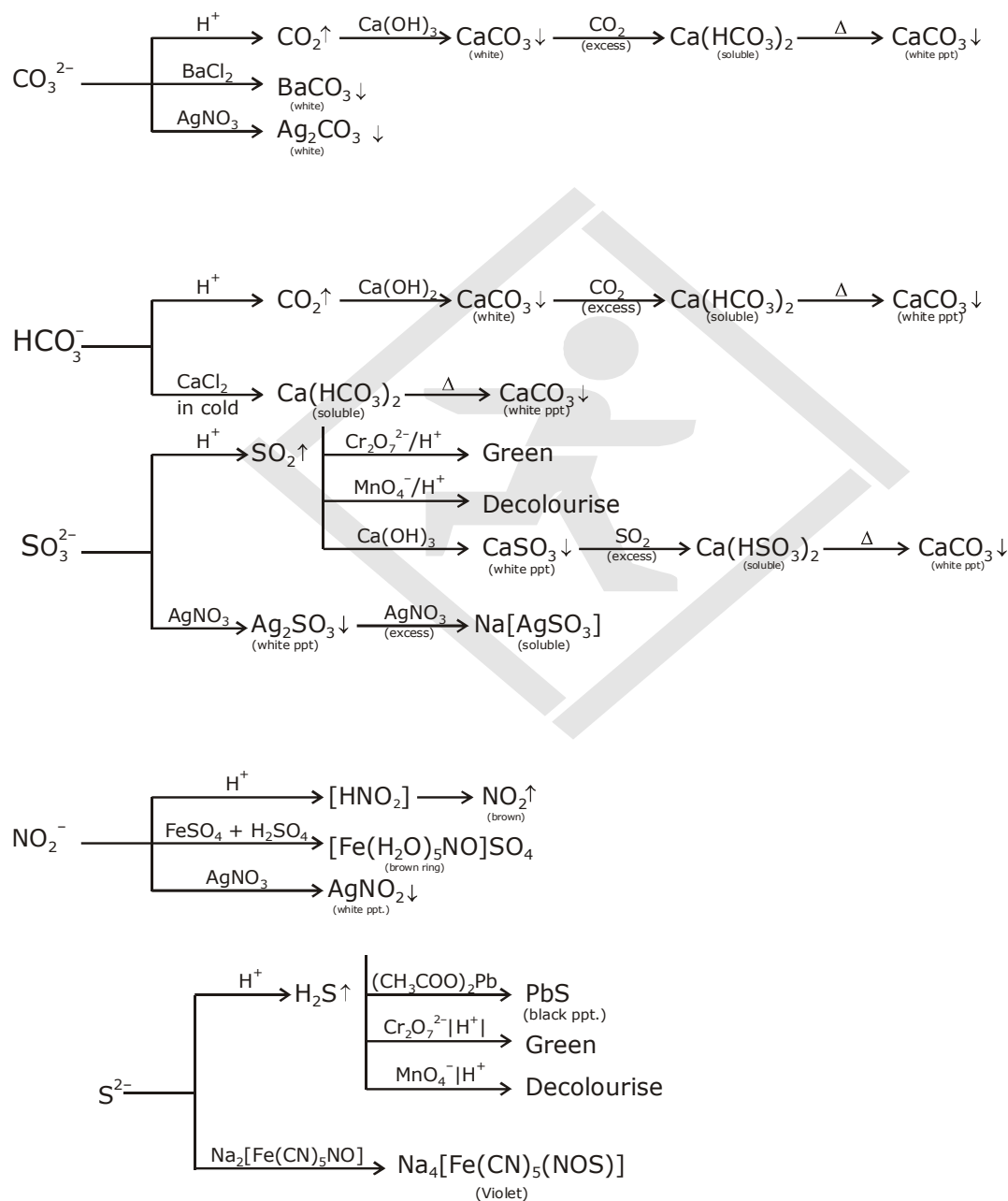
Qualitative analysis involves identification of ions (cations and anion) of a salt or a mixture of salts through their characteristic reactions. The process involves.

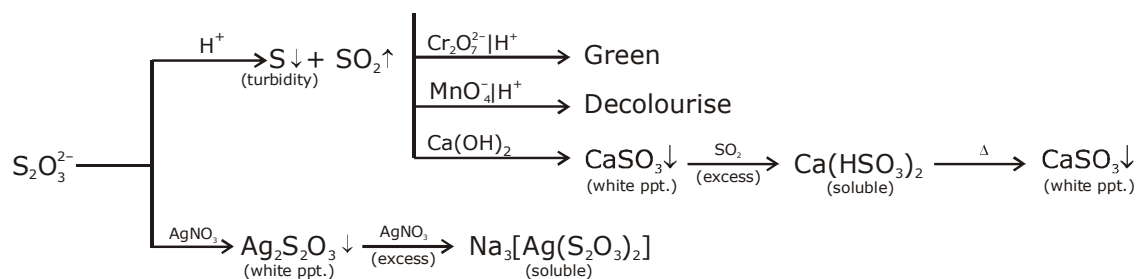
- (i) Analysis of anions and
- (ii) Analysis of cations.

ANALYSIS OF ANIONS (ACIDIC RADICALS)

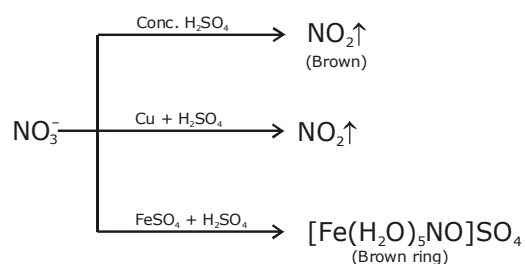
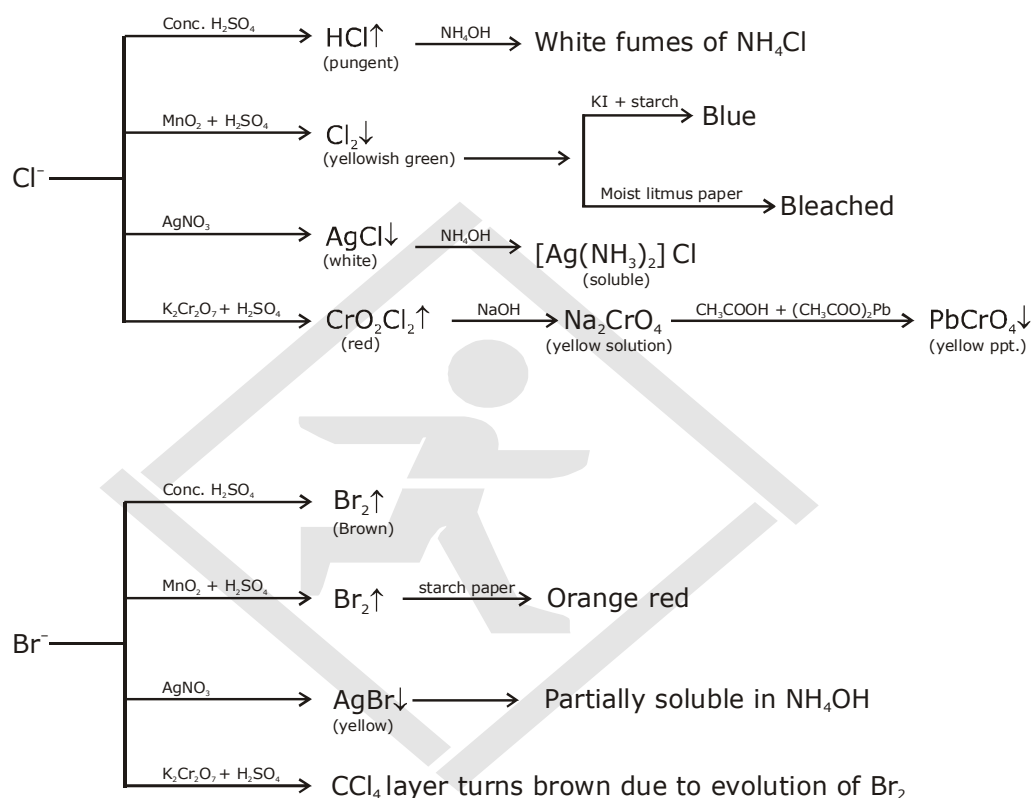
Group I Anions which liberate gases with dil. HCl or dil. H_2SO_4

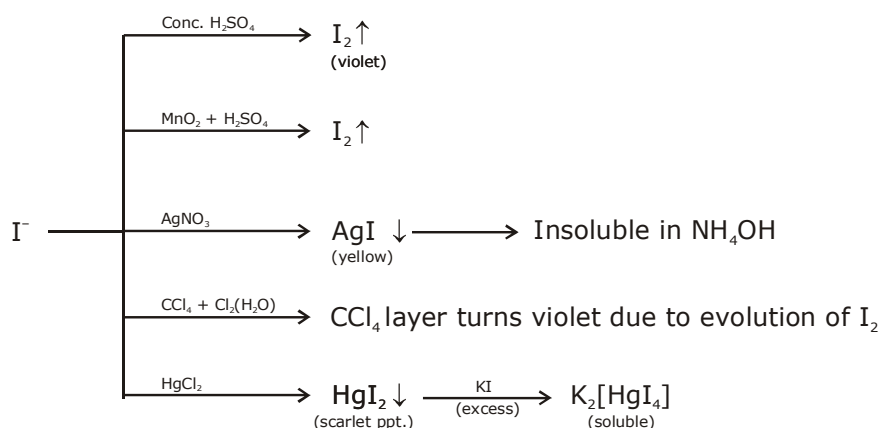
$(\text{CO}_3^{2-}, \text{HCO}_3^-, \text{SO}_3^{2-}, \text{S}^{2-}, \text{S}_2\text{O}_3^{2-}, \text{NO}_2^-)$



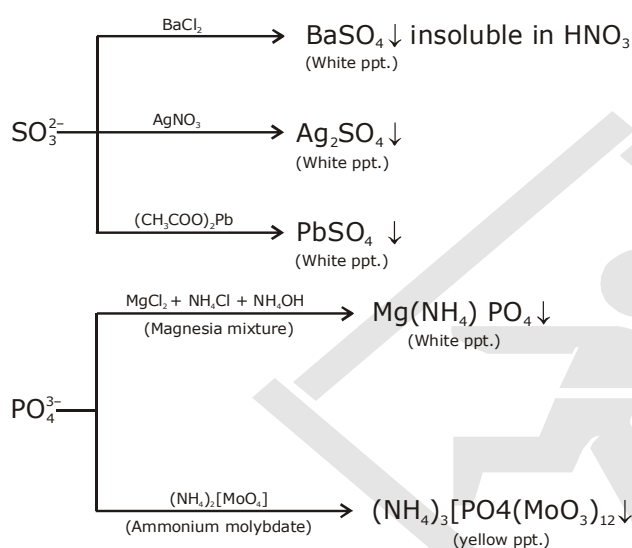


Group II: Gases or acid vapours evolved with conc. H_2SO_4 (Cl^- , Br^- , I^- , NO_3^-)



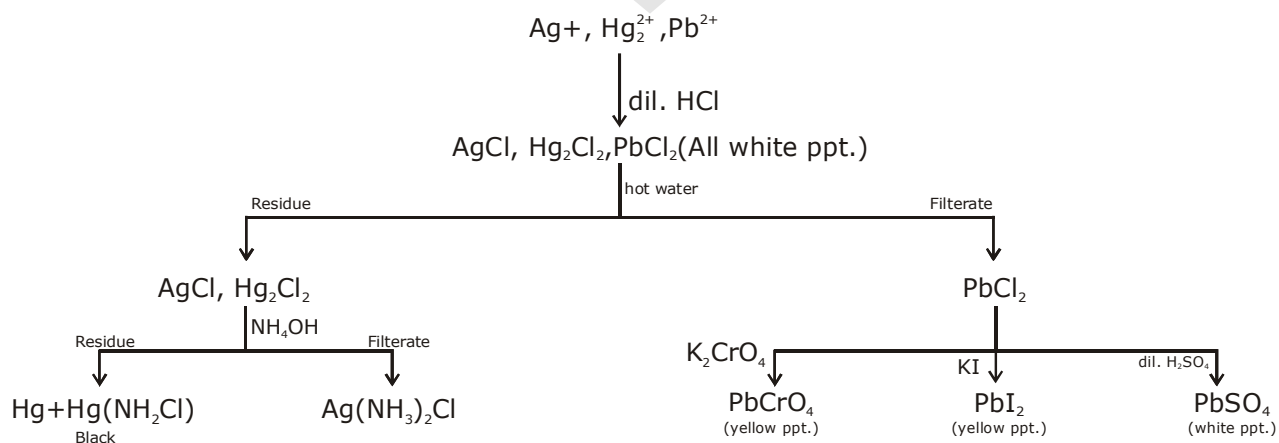


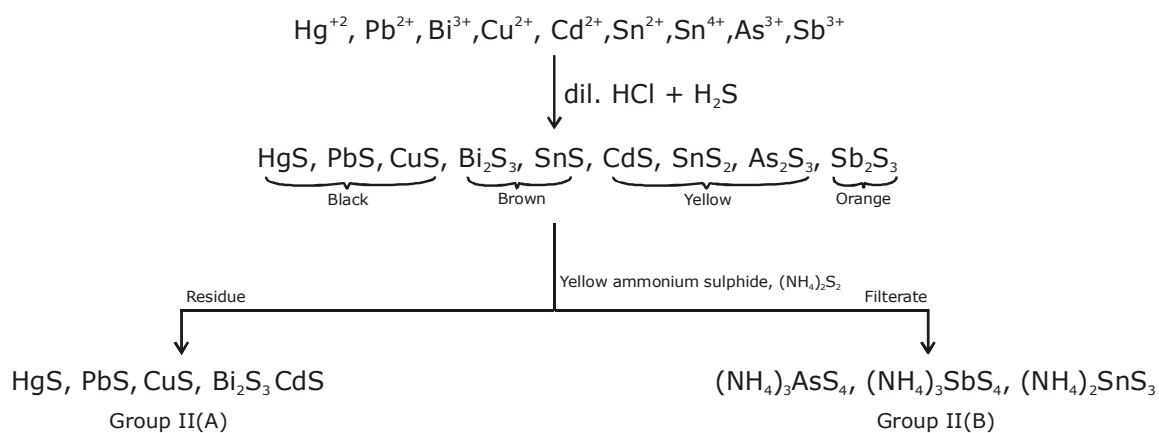
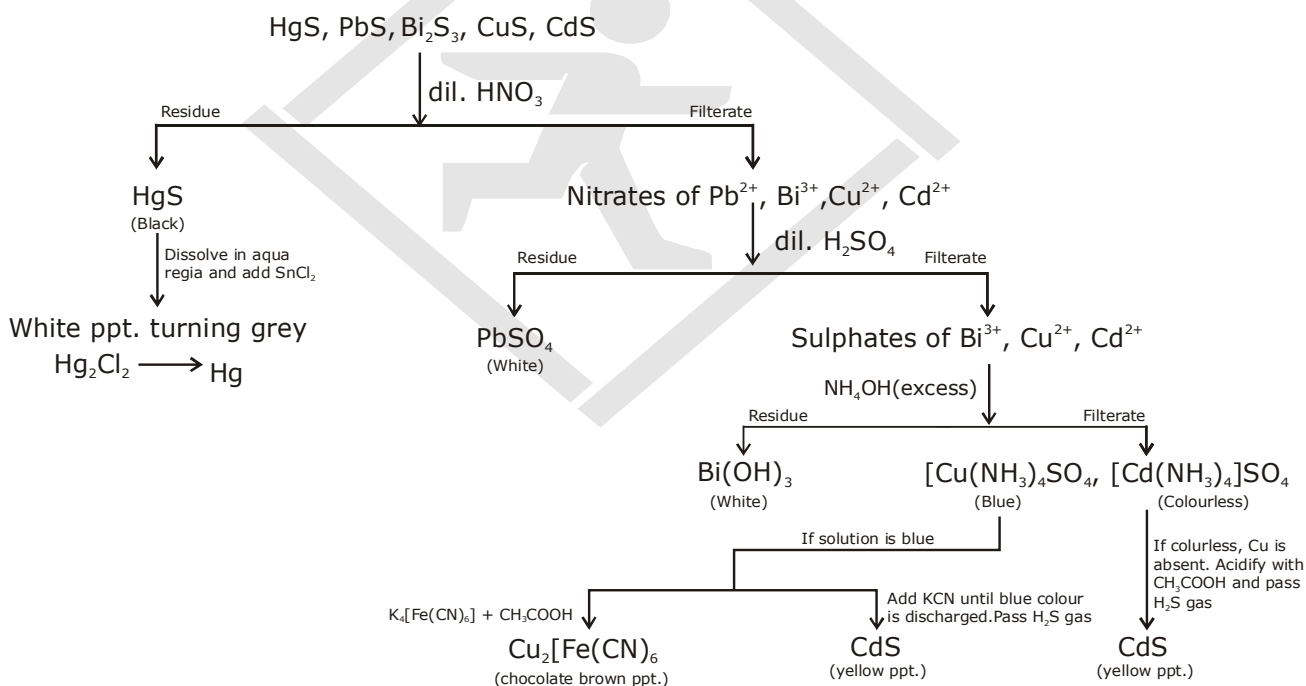
Group III : Anions which do not liberate any gas with dil HCl or conc. H_2SO_4 . They are detected by precipitation (SO_4^{2-} , PO_4^{3-}).

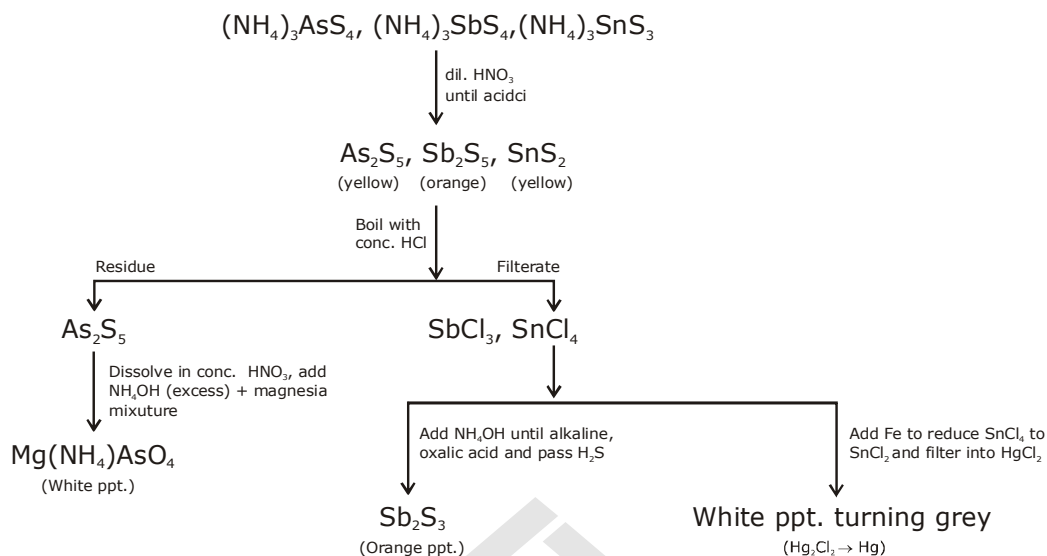
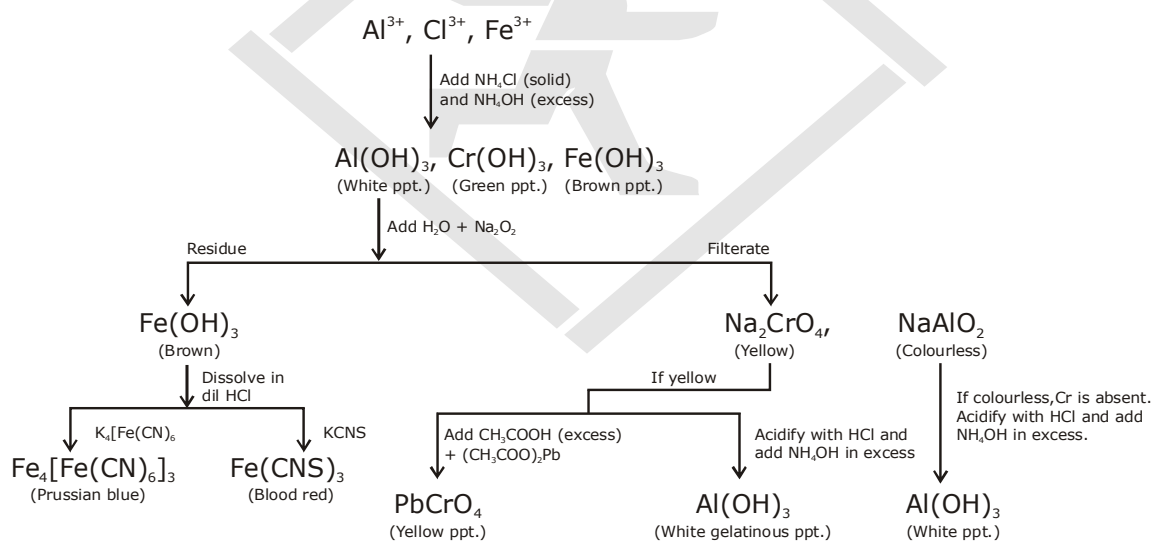


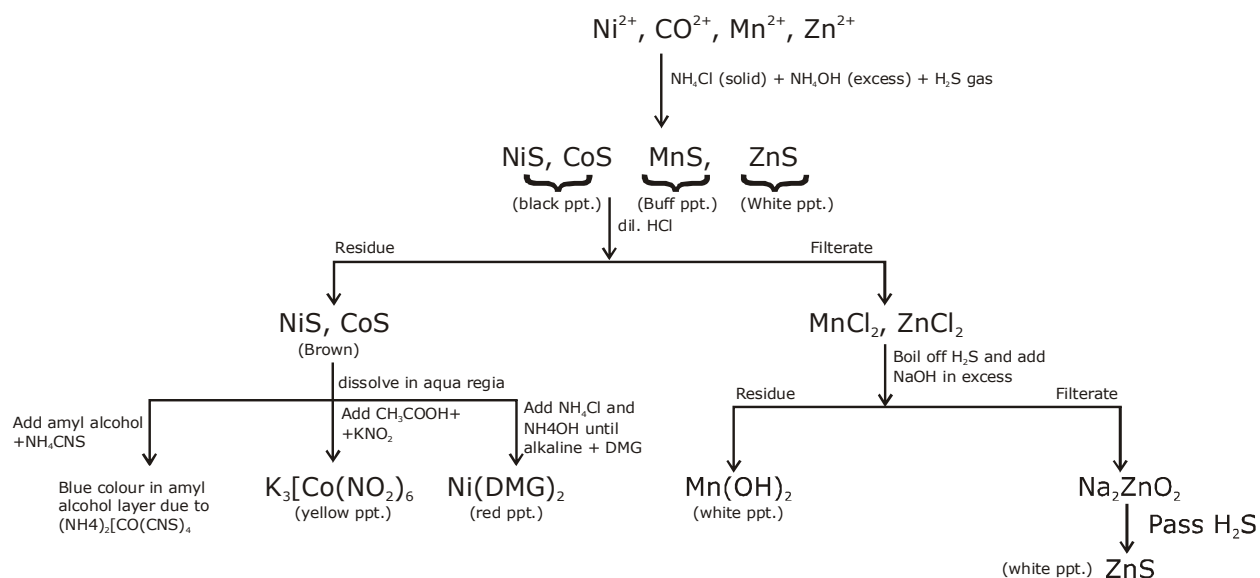
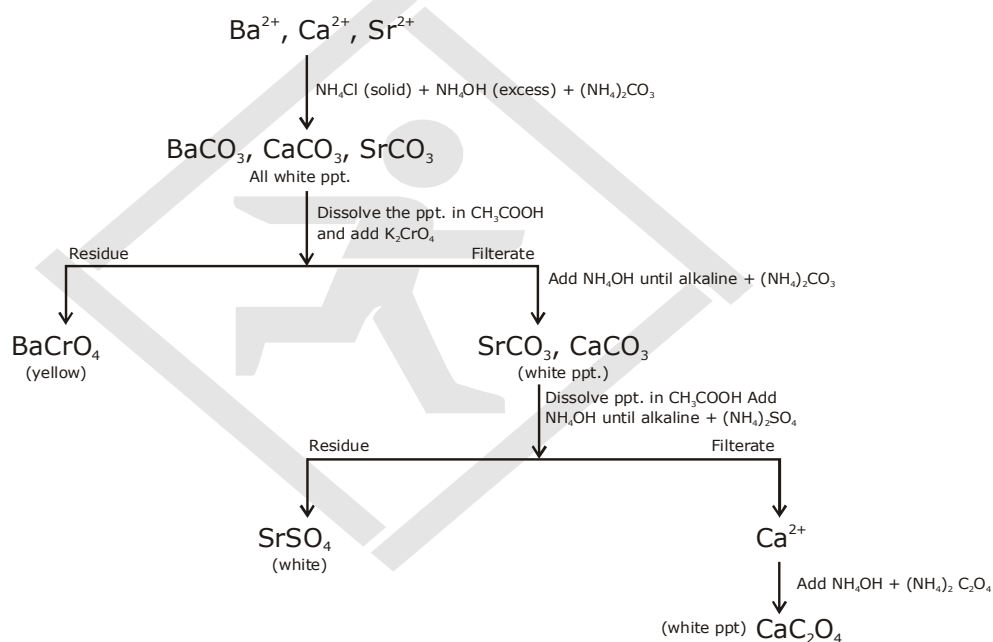
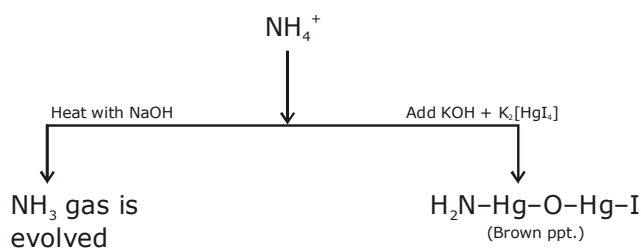
ANALYSIS OF CATIONS (BASIC RADICALS)

Group I



Group II**Group II(A)**

Group II(B)**Group III**

Group IV**Group V****Group VI**

Principles of qualitative analysis group I to V excluding interfering radicals.

The detection of cations (basic radicals) and anions (acidic radicals) in a salt or in a mixture is known as **Qualitative Analysis**.

Some Important Observations during Qualitative Analysis**1. List of different coloured salts**

Salts	Colour
Copper salts	Bluish green
Nickel salts	Greenish blue
Chromium salts	Dark green
Cobalt salts	Pinkish or purple
Manganese salts	Light pink
Ferrous salts	Light green
Ferric salts	Pale yellow

2. Action of Heat (Colour of Residue)

S. No.	Colour	Residue
i)	Yellow (hot) and white (cold)	ZnO
ii)	Reddish brown (hot) and yellow (cold)	PbO
iii)	Black (hot) and Red (cold)	HgO , Pb_3O_4
iv)	Black (hot) and Red brown (cold)	Fe_2O_3
v)	Decipitation	$\text{Pb}(\text{NO}_3)_2$, NaCl
vi)	White sublimate	Ammonium salts

3. Gases

S. No.	Nature	Gases
i)	Colourless and odourless gases	O_2 , CO_2 , N_2
ii)	Colourless gases with odour	NH_3 , SO_2 , HCl , H_2S
iii)	Coloured gases	NO_2 (brown), Br_2 , (reddish brown), I_2 (violet) Cl_2 (greenish yellow)

4. Flame Test

Metals	Colour
Li	crimson red
Na	golden yellow
K	violet
Ca	Brick red
Sr	crimson
Ba	apple green

Classification Of Anions

Methods available for the detection of anions are not as systematic as those used for the detection of cations. Furthermore anions are classified essentially on the basis of process employed.

Class A: Includes anions that are identified by volatile products obtained on treatment with acids. It is further divided into two sub groups.

- (i) Gases evolved with dil HCl/ dil H_2SO_4 .
- (ii) Gases or acid vapours evolved with conc H_2SO_4

Class B: Includes anions that are identified by their reactions in solution. It is subdivided into two groups:

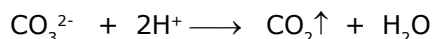
- (i) Precipitation reactions
- (ii) Oxidation and reduction in solution

Class A (i): Anions which evolve gases on reaction with dil. HCl/dil. H_2SO_4 .

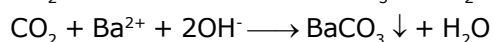
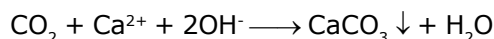
It includes - CO_3^{2-} , SO_3^{2-} , S^{2-} , NO_2^- , CH_3COO^- , $\text{S}_2\text{O}_3^{2-}$

1. Carbonate (CO_3^{2-}) :

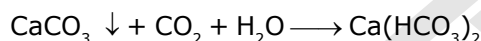
(i) **Dilute HCl** : gives effervescence, due to the evolution of carbon dioxide



The gas gives *white turbidity* with *lime water* and *baryta water*

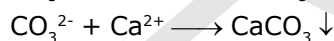
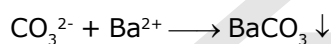


On prolonged passage of carbon dioxide in lime water, the turbidity slowly disappears due to the formation of soluble hydrogen carbonate.

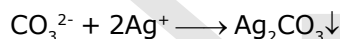


The following tests performed with then aqueous salts solution.

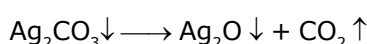
(ii) **Barium chloride or Calcium chloride solution:** White ppt of barium or Calcium carbonate is obtained, which is soluble in mineral acid.



(iii) **Silver nitrate solution** : White ppt of silver carbonate is obtained.

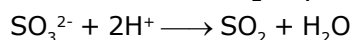


The ppt so obtained is soluble in nitric acid and in ammonia, the ppt becomes *yellow or brown* on addition of excess reagent and same may also be happened if the mix is boiled, due to the formation of silver oxide



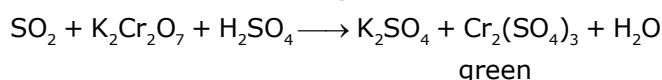
2. Sulphites (SO_3^{2-}):

(i) **Dilute HCl or Dilute H_2SO_4** : decomposes with the evolution of sulphur dioxide

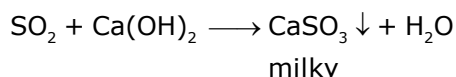


The gas has a *suffocating odour* of burning sulphur.

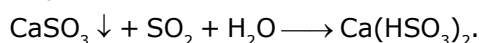
(ii) **Acidified potassium dichromate solution:** The gas turns filter paper moistened with acidified potassium dichromate solution, green due to the formation of Cr^{3+} ions.



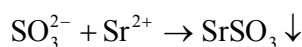
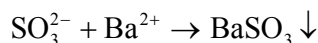
(iii) **Lime water** : On passing the gas through lime water, a milky ppt is formed.



Precipitate dissolves on prolonged passage of the gas, due to the formation of soluble hydrogen sulphite ions.

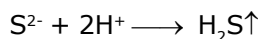


(iv) **Barium chloride or Strontium chloride solution** : Salt solutions gives *white ppt* of barium or strontium sulphite.

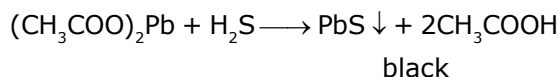


3. Sulphide (S^{2-}) :

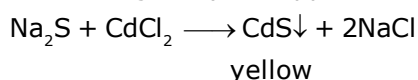
(i) **Dil HCl or Dil H_2SO_4** : A colourless gas with a smell of rotten eggs (H_2S) is evolved



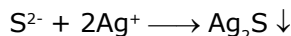
(ii) The gas turns lead acetate paper *black*



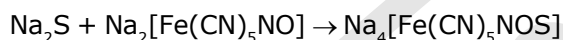
(iii) Salt solution gives yellow *ppt.* with CdCl_2



(iv) **Silver nitrate solution** : black ppt. of silver sulphide insoluble in cold but soluble in hot dil nitric acid.

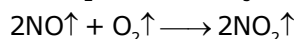
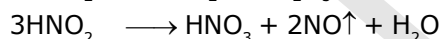
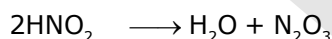
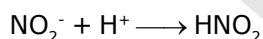


(v) **Sodium nitroprusside solution** : Turns sodium nitroprusside solution *purple*



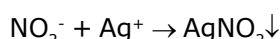
4. Nitrites (NO_2^-) :

(i) **Dil HCl and Dil. H_2SO_4** : Adding to solid nitrite in cold yield *pale blue liquid* (due to the presence of free nitrous acid HNO_2 or its anhydride N_2O_3) & the evolution of *brown fumes* of nitrogen dioxide, the latter being largely produced by combination of nitric oxide with the oxygen of the air

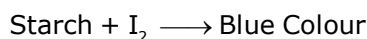
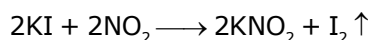


Following tests performed with an aqueous salt solution.

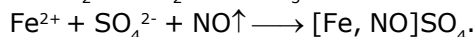
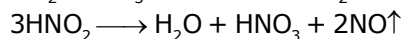
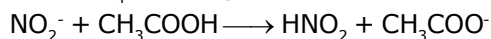
(ii) **Silver nitrate solution** : *White* crystalline ppt. is obtained



(iii) Turns acidified KI - starch paper *blue*

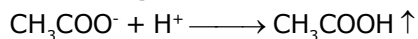


(iv) **Brown ring test**: When the nitrite solution is added carefully to a conc. solution of Iron(II) sulphate acidified with dil acetic acid or with dilute sulphuric acid, a **brown ring**, due to the formation of $[\text{Fe}, \text{NO}]\text{SO}_4$ at the junction of the two liquids.

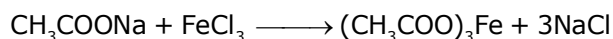


5. Acetate (CH_3COO^-) :

(i) **Dilute Sulphuric Acid**: Smell of vinegar



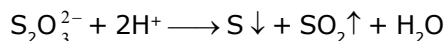
- (ii) **Iron (III) Chloride Solution:** Gives deep - red colouration



Brown colour

6. **Thiosulphates ($\text{S}_2\text{O}_3^{2-}$):**

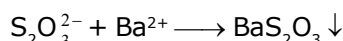
- (i) **Dil Hydrochloric acid :** Gives sulphur & sulphur di oxide



- (ii) **Iodine Solution :** Decolourise due to formation of tetrathionate ion

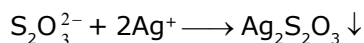


- (iii) **Barium chloride solution :** White ppt. of barium thiosulphate is formed

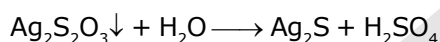


But no ppt. is obtained with CaCl_2 solution.

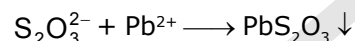
- (iv) **Silver nitrate solution :** Gives white ppt. of silver thiosulphate.



The ppt. is unstable, turning dark on standing, due to the formation of silver sulphide.



- (v) **Lead acetate or Lead nitrate solution :** Gives white ppt.



On boiling it turns black due to the formation of PbS .

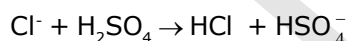


Class A(ii): Gases or acid vapours evolved with conc. Sulphuric acid

It includes - Cl^- , Br^- , I^- , NO_3^- .

1. **Chloride (Cl^-) :**

- (i) **Conc. H_2SO_4 :** decomposes with the evolution of HCl .



Gas so produced

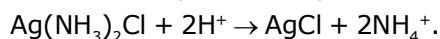
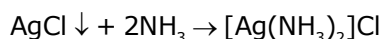
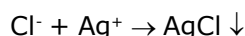
- Turns blue litmus paper red
- Gives *white fumes* of NH_4Cl when a glass rod moistened with ammonia solution is brought to the mouth of test tube.

- (ii) **Manganese dioxide and conc. sulphuric acid:** When a solid chloride is treated with MnO_2 and conc. H_2SO_4 , *yellowish green colour* is obtained.

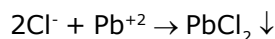


The following tests are performed with the salt solution.

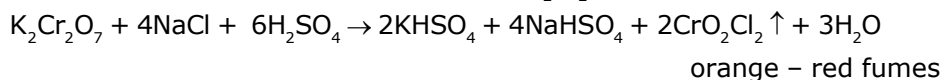
- (iii) **Silver nitrate solution:** *White, curdy ppt.* of AgCl insoluble in water & in dil nitric acid, but soluble in dilute ammonia solution.



- (iv) **Lead acetate solution:** *White ppt.* of lead chloride is formed

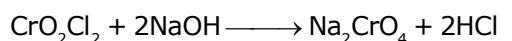


(v) **Chromyl chloride test** : When a mix containing chloride ion is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 orange red fumes of chromyl chloride (CrO_2Cl_2) are formed.

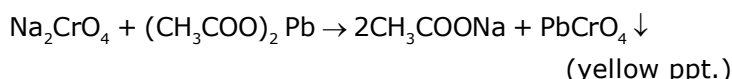


Chlorides of mercury, owing to their slight ionization, do not respond to this test and only partial conversion to CrO_2Cl_2 occurs with the chlorides of lead, silver, antimony and tin.

When chromyl chloride vapours are passed into sodium hydroxide a yellow solution of sodium chromate is formed which when treated with lead acetate gives yellow ppt. of lead chromate.

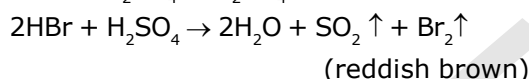
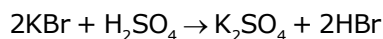


Yellow solution



2. Bromide (Br^-)

(i) **Conc. H_2SO_4** : Gives reddish brown vapours of bromine.

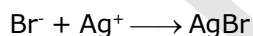


(ii) **Manganese dioxide and conc. sulphuric acid** : When a mix of solid bromide, MnO_2 and conc. H_2SO_4 is heated reddish brown vapours of bromine are evolved.

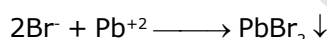


The following tests are performed with the salt solution.

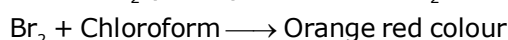
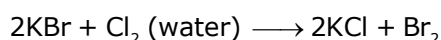
(iii) **Silver nitrate solution**: A pale yellow ppt. of silver bromide is obtained. This ppt. is sparingly soluble in dil but readily soluble in conc. ammonia solution and insoluble in dil. HNO_3 .



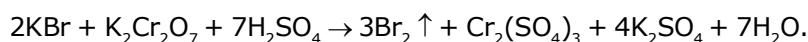
(iv) **Lead acetate solution**: White crystalline ppt. of lead bromide which is soluble in boiling water.



(v) **Chlorine water**: When this solution is added to a solution of bromide and chloroform free bromine is liberated, which colours the organic layer orange – red.

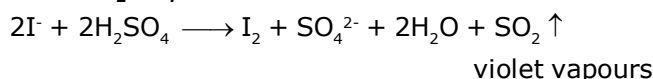


(vi) **Potassium dichromate & conc. H_2SO_4** : When a mix of solid bromide, $K_2Cr_2O_7$, and conc. H_2SO_4 is heated and passing the evolved vapours into water, a yellowish brown solution is obtained.



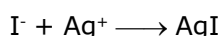
3. Iodide (I^-) :

(i) **Conc. H_2SO_4** : Gives violet vapours of iodine

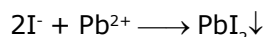


The following tests are performed with the salt solution.

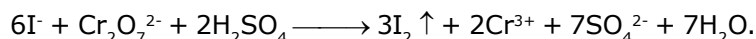
(ii) **Silver nitrate solution**: Yellow, curdy ppt. of silver iodide AgI , very slightly soluble in conc. ammonia solution and insoluble in dil nitric acid.



(iii) **Lead acetate solution:** Yellow, curdy ppt. of lead iodide soluble in much hot water forming a colourless solution & yielding golden yellow plates (*spangles*) on cooling.



(iv) **Potassium dichromate & conc. sulphuric acid:** Iodine is liberated

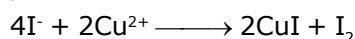


(v) **Chlorine water:** Iodine is liberated, by the dropwise addition of chlorine water to iodide, and on addition of CHCl_3 violet coloured organic layer is obtained.

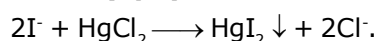


I_2 + chloroform \longrightarrow violet coloured layer.

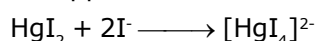
(vi) **Copper sulphate solution:** Gives brown ppt. consisting of a mixture of copper (I) iodide & iodine and on addition of hypo solution brown ppt changes to white ppt.



v(ii) **Mercury (II) chloride solution:** Forms scarlet ppt. of HgI_2

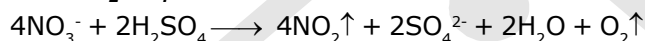


This ppt. dissolves in excess of KI, forming tetraiodo mercurate (II) complex.



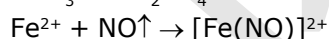
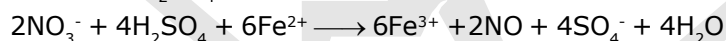
4. Nitrate (NO_3^-) :

(i) **Conc H_2SO_4 :** Gives reddish - brown vapours of nitrogen dioxide



The following tests are performed with the salt solution.

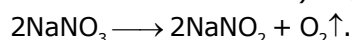
(ii) **Brown ring test :** When a freshly prepared solution of iron (II) sulphate is added to nitrate solution & conc. H_2SO_4 is poured slowly down the side of the test - tube, a brown ring is obtained.



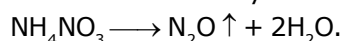
On shaking and warming the mix, the brown colour disappears, nitric oxide is evolved and a yellow solution of Iron(III) ions remains.

Action of heat : The result varies with the metal

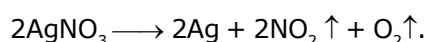
1. Nitrates of sodium and potassium evolve oxygen (*test with glowing splint*) & leave solid nitrites (brown fumes with dilute acid)



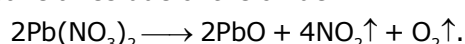
2. Ammonium nitrate yields dinitrogen oxide & steam



3. Nitrates of the noble metals leave a residue of the metal and a mix of nitrogen dioxide and oxygen is evolved.



4. Nitrates of other metals, such as those of lead and copper, evolve oxygen and nitrogen dioxide and leave a residue of the oxide.



Class B

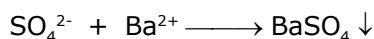
(i) Precipitation reaction : SO_4^{2-}

(ii) Oxidation and reduction in solution - CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, MnO_4^-

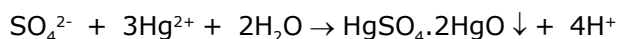
1. **Sulphate (SO_4^{2-}):**

All sulphates except those of Ba, Pb, Sr are soluble in water. Sulphates of calcium and mercury(II) are slightly soluble. The following tests are performed with the salt solution.

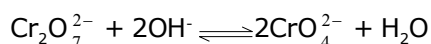
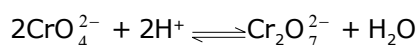
(i) **Barium chloride solution:** White ppt. of barium sulphate BaSO_4 insoluble in warm dil. hydrochloric acid and in dilute nitric acid, but moderately soluble in boiling, conc. hydrochloric acid.



(ii) **Mercury (II) nitrate solution :** Gives yellow ppt. of basic mercury (II) sulphate.

2. **Chromate CrO_4^{2-} and Dichromate ($\text{Cr}_2\text{O}_7^{2-}$) :**

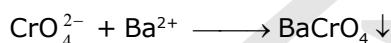
Metallic chromates gives *yellow solution* when dissolved in water. In the presence of H^+ chromates are converted into dichromates (orange-red solution).



It may also be expressed as :



(i) **Barium chloride solution:** *Pale - yellow ppt.* of barium chromate soluble in dilute mineral acids but insoluble in water and acetic acid.

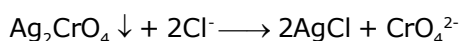
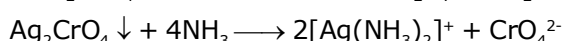
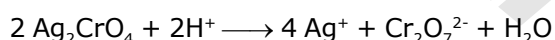
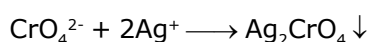


Dichromate ions also gives the same ppt. but due to the formation of strong acid precipitation is partial.

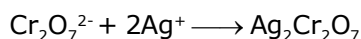


If sodium hydroxide or sodium acetate is added, precipitation becomes quantitative.

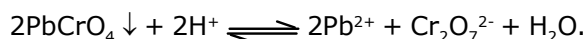
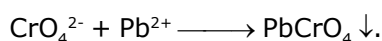
(ii) **Silver nitrate solution:** *Brownish - red ppt.* of silver chromate Ag_2CrO_4 which is soluble in dil. nitric acid & in ammonia solution, but is insoluble in acetic acid.



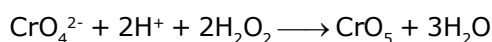
A reddish brown ppt. of silver dichromate $\text{Ag}_2\text{Cr}_2\text{O}_7$ is formed with a conc. solution of a dichromate.



(iii) **Lead acetate solution:** *Yellow ppt.* of lead chromate PbCrO_4 insoluble in acetic acid, but soluble in dil nitric acid



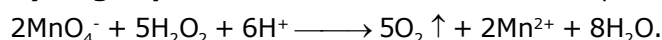
(iv) **H_2O_2 :** If an acidic solution of a chromate is treated with H_2O_2 a *deep blue solution* of chromium penta oxide is obtained.



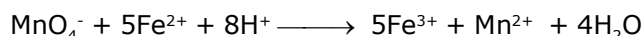
CrO_5 is unstable and it decomposes yielding oxygen and a *green solution* of a Cr^{+3} Salt.

3. Permanganate MnO_4^- :

(i) **Hydrogen peroxide** : It decolourises acidified potassium permanganate solution



(ii) Iron (II) sulphate, in the presence of sulphuric acid, reduces permanganate to manganese (II). The solution becomes *yellow* because of the formation of iron (III) ions



(iii) **Action of heat** : On heating, a residue of potassium manganate K_2MnO_4 and black manganese dioxide remains behind. Upon extracting with water and filtering, a green solution of potassium manganate is obtained.



Exercise 1: (i) **How to distinguish between CO_3^{2-} and SO_3^{2-} ions?**

(ii) **A gas turns red litmus paper into blue and forms white fume with HCl, identify the gas**

Classification of Cations

For the purpose of systematic qualitative analysis, cations are classified into *five groups* on the basis of their behaviour with some reagents and classification is based on whether a cation reacts with these reagents by the formation of precipitate or not (solubility difference)

Group reagent: Hydrochloric acid, hydrogen sulphide, ammonium sulphide and ammonium carbonate.

Group	Group Reagent	Ions	Colour & Ppt.
Group I	dil HCl	Pb^{2+} , Hg^+ , Ag^+	PbCl_2 , Hg_2Cl_2 , AgCl - white
Group II Group II A	H_2S in dil HCl	Hg^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+} As^{3+} , As^{5+} , Sb^{3+} , Sb^{5+} , Sn^{2+} ,	Yellow- CdS , As_2S_3 , As_2S_5 , SnS_2
Group II B		Sn^{4+}	Black - HgS , CuS , PbS Orange - Sb_2S_3 , Sb_2S_5 Brown - Bi_2S_3 , SnS
Group III A	NH_4OH in presence of NH_4Cl	Fe^{3+} , Al^{3+} , Cr^{3+}	$\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$ Brown White Green
Group III B	H_2S in presence of NH_3 & NH_4Cl or NH_4S .	Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+}	ZnS - white or grey, Black - CoS , NiS MnS - Buff (light pink)
Group IV	$(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4Cl & NH_4OH .	Ba^{2+} , Sr^{2+} , Ca^{2+}	BaCO_3 , SrCO_3 , CaCO_3 - white
Group V	No common group reagent.	Mg^{2+} , Na^+ , K^+ , NH_4^+	—

Points to Remember

- Group I radicals (Ag^+ , Pb^{+2} , Hg_2^{+2}) are precipitated as chlorides because the solubility product of these chlorides (AgCl , PbCl_2 , Hg_2Cl_2) is less than the solubility products of all other chlorides which remain in solution.
- Group II radicals are precipitated as sulphides because sulphides of other metals remain in solution because of their high solubility products, HCl acts as a source of H^+ and thus decreases the conc. of S^{2-} due to *common ion effect*. Hence decreased conc. of S^{2-} is only sufficient to precipitate the Group II radicals only.
- Group III A radicals are precipitated as hydroxides and the NH_4Cl suppresses the ionisation of NH_4OH so that only the group III A radicals are precipitated because of their low solubility product.

Note:

- Excess of NH_4Cl should be added otherwise manganese will be ppt. as $\text{MnO}_2 \cdot \text{H}_2\text{O}$.
- $(\text{NH}_4)_2\text{SO}_4$ can't be used in place of NH_4Cl because the SO_4^{2-} will ppt. barium as BaSO_4 .
- NH_4NO_3 can't be used in place of NH_4Cl because NO_3^- ions will oxidise Mn^{2+} to Mn^{3+} and thus $\text{Mn}(\text{OH})_3$ will be precipitated in III A group.
- Only $\text{Al}(\text{OH})_3$ is soluble in excess of NaOH followed by boiling to form sodium metaluminate while $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ are insoluble.

- Ammonium hydroxide increases the ionisation of H_2S by removing H^+ from H_2S as unionised water

$$\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-} \quad \text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$$
 Now excess of S^{2-} ions are available and hence the ionic product of hydroxides of Group III B exceed their solubility product and ppt. will be obtained. In case H_2S is passed through a neutral solution, incomplete precipitation will take place due to the formation of HCl which decreases the ionization of H_2S .

$$\text{MnCl}_2 + \text{H}_2\text{S} \longrightarrow \text{MnS} + 2\text{HCl}$$

Identification of Basic Radicals

All confirmatory tests for basic radicals are performed with the salt solution.

1. Group I (Pb^{2+} , Ag^+ , Hg^+)

- PbCl_2 gives a yellow ppt. with K_2CrO_4 . The ppt. is insoluble in acetic acid but soluble in NaOH

$$\text{Pb}(\text{NO}_3)_2 + \text{K}_2\text{CrO}_4 \rightarrow \text{PbCrO}_4 \downarrow + 2\text{KNO}_3$$

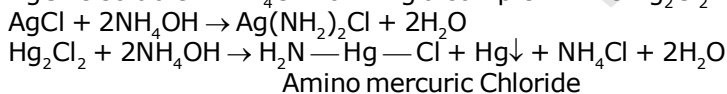
Yellow ppt.

$$\text{PbCrO}_4 + 4\text{NaOH} \rightarrow \text{Na}_2[\text{PbO}_2] + \text{Na}_2\text{CrO}_4 + 2\text{H}_2\text{O}$$
- $\text{Pb}(\text{NO}_3)_2 + 2\text{KI} \rightarrow \text{PbI}_2 \downarrow + 2\text{KNO}_3$

(Yellow)

$$\text{PbCl}_2 + 2\text{KI} (\text{excess}) \rightarrow \text{K}_2[\text{PbI}_4]$$

- AgCl is soluble in NH_4OH forming a complex while Hg_2Cl_2 forms a *black ppt.* with NH_4OH .

**2. Group II A (Hg^{2+} , Cu^{2+} , Bi^{3+} , Cd^{2+})**

- Hg^{+2} ions in solution, on addition of SnCl_2 , give *white precipitate* turning *black*.

$$2\text{Hg}^{+2} + \text{SnCl}_2 \rightarrow \text{Sn}^{+4} + \text{Hg}_2\text{Cl}_2 \downarrow$$

White

$$\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \rightarrow \text{SnCl}_4 + 2\text{Hg} \downarrow$$

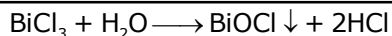
Black
- Cu^{+2} ions in solution gives a pale blue precipitate which gives a deep blue colour with excess of NH_4OH

$$\text{Cu}^{+2} + 4\text{NH}_4\text{OH} \rightarrow [\text{Cu}(\text{NH}_3)_4]^{+2} + 4\text{H}_2\text{O}$$

Deep blue in colour

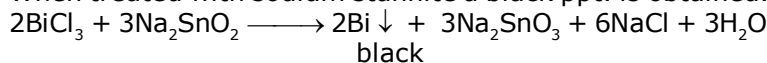
$$\text{Cu}^{+2} \text{ ions give chocolate precipitate with } \text{K}_4\text{Fe}(\text{CN})_6.$$

$$2\text{Cu}^{+2} + \text{K}_4\text{Fe}(\text{CN})_6 \rightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 4\text{K}^+$$
- Bi^{+3} ions in solution of HCl on addition of water give white cloudy precipitate.

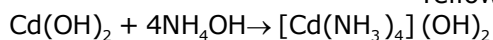
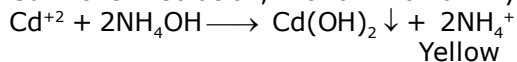


White ppt.

When treated with sodium stannite a black ppt. is obtained.

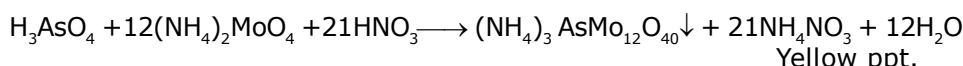
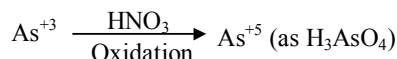


- (iv) Cd^{+2} ions in solution, with ammonium hydroxide gives a white precipitate which dissolves.

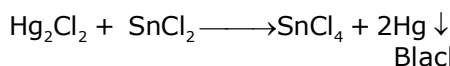
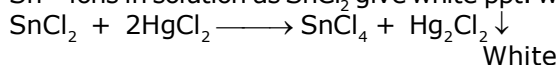


3. Group II B (As^{3+} , As^{5+} , Sb^{3+} , Sb^{5+} , Sn^{3+} , Sn^{4+})

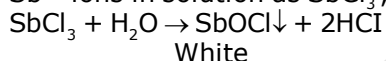
- (v) As^{+3} ions in solution give *yellow precipitate* with ammonium molybdate and HNO_3 .



- (vi) Sn^{+2} ions in solution as SnCl_2 give white ppt. with HgCl_2 , which turns black on standing.

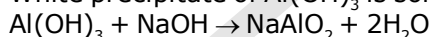


- v(ii) Sb^{+3} ions in solution as SbCl_3 , on addition of water give white precipitate.

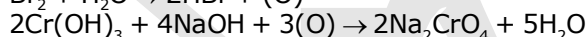


4. Group III A (Al^{3+} , Fe^{3+} , Cr^{3+})

- (i) White precipitate of $\text{Al}(\text{OH})_3$ is soluble in NaOH



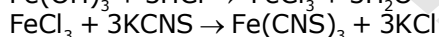
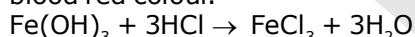
- (ii) Precipitate of $\text{Cr}(\text{OH})_3$ is soluble in $\text{NaOH} + \text{Br}_2$ water and addition of BaCl_2 to this solution gives yellow precipitate.



Yellow ppt.

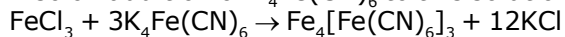
$\text{Fe}(\text{OH})_3$ is insoluble in NaOH

- (iii) Brown precipitate of $\text{Fe}(\text{OH})_3$ is dissolved in HCl and addition of KCNS to this solution gives blood red colour.



blood red

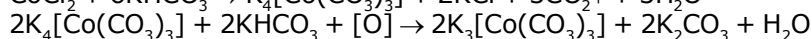
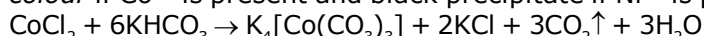
Also on addition of $\text{K}_4\text{Fe}(\text{CN})_6$ to this solution, a prussian blue colour is obtained.



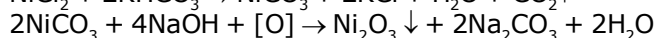
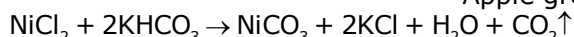
prussian blue colour

5. Group III B (Ni^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+})

- (i) Ni^{+2} and Co^{+2} ions in solution, on addition of KHCO_3 and Br_2 water give *apple green colour* if Co^{+2} is present and black precipitate if Ni^{+2} is present.



Apple green colour



Black ppt.

- (ii) Zn^{+2} ions in solution give a *white precipitate* with NaOH, which dissolves in excess of NaOH.

$$\text{Zn}^{+2} + 2\text{NaOH} \rightarrow \text{Zn}(\text{OH})_2 \downarrow + 2\text{Na}^+$$
White

$$\text{Zn}(\text{OH})_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$$
Soluble
- (iii) Mn^{+2} ions in solution give *pink precipitate* with NaOH turning *black* or *brown* on heating.

$$\text{Mn}^{+2} + 2\text{NaOH} \longrightarrow \text{Mn}(\text{OH})_2 + 2\text{Na}^+$$
Pink

$$\text{Mn}(\text{OH})_2 + [\text{O}] \xrightarrow{\Delta} \text{MnO}_2 + \text{H}_2\text{O}$$
Brown or black

6. Group IV (Ba^{2+} , Sr^{2+} , Ca^{2+})

- (i) Ba^{+2} ions in solution give
- (a) *Yellow precipitate* with K_2CrO_4

$$\text{Ba}^{+2} + \text{K}_2\text{CrO}_4 \rightarrow \text{BaCrO}_4 \downarrow + 2\text{K}^+$$
Yellow
- (b) *White precipitate* with $(\text{NH}_4)_2\text{SO}_4$

$$\text{Ba}^{+2} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NH}_4^+$$
White
- (c) *White precipitate* with $(\text{NH}_4)_2\text{C}_2\text{O}_4$

$$\text{Ba}^{+2} + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{BaC}_2\text{O}_4 \downarrow + 2\text{NH}_4^+$$
White
- (ii) Sr^{+2} ions give white precipitate with $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$

$$\text{Sr}^{+2} + (\text{NH}_4)_2\text{SO}_4 \rightarrow \text{SrSO}_4 \downarrow + 2\text{NH}_4^+$$
White ppt.

$$\text{Sr}^{+2} + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{SrC}_2\text{O}_4 \downarrow + 2\text{NH}_4^+$$
White
- (iii) Ca^{+2} ions give *white precipitate* with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ only.

$$\text{Ca}^{+2} + (\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + 2\text{NH}_4^+$$
White

7. Group V (NH_4^+ , Na^+ , K^+ , Mg^{+2})

- (i) All ammonium salts on heating with alkali say NaOH give a colourless, pungent smelling gas (NH_3).

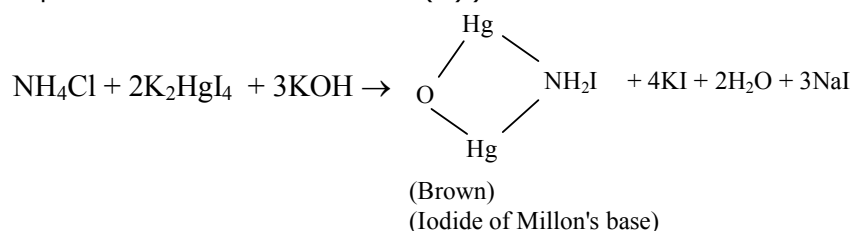
$$\text{NH}_4\text{Cl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{NH}_3 \uparrow + \text{H}_2\text{O}$$
- (a) Gas evolved gives white fumes with a rod dipped in conc. HCl

$$\text{NH}_3 + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} \uparrow$$
White fumes
- (b) Paper soaked in CuSO_4 solution, becomes deep blue due to complex formation with NH_3 .

$$\text{CuSO}_4 + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$$
deep blue
- (c) With $\text{Hg}_2(\text{NO}_3)_2$, a *black colour* is obtained

$$\text{Hg}_2(\text{NO}_3)_2 + 2\text{NH}_3 \longrightarrow \text{Hg} \downarrow + \text{Hg}(\text{NH}_2)\text{NO}_3 \downarrow + \text{NH}_4\text{NO}_3$$
black
- (d) An aqueous solution of an ammonium gives a brown ppt. with Nessler's reagent(alkaline solution

of potassium tetraiodomercurate(II)).



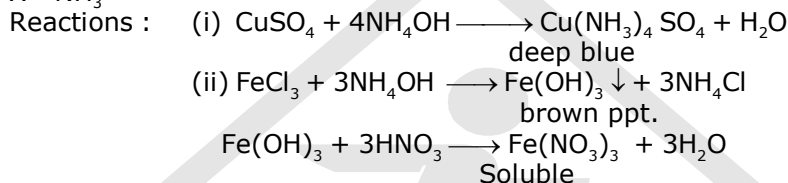
- (ii) Potassium salts give a *yellow ppt.* with sodium cobaltinitrite
 $\text{Na}_3[\text{Co}(\text{NO}_2)_6] + 3\text{KCl} \longrightarrow \text{K}_3[\text{Co}(\text{NO}_2)_6] + 3\text{NaCl}$
yellow
- (iii) Sodium salts give a heavy white ppt. with potassium dihydrogen antimonate
 $\text{KH}_2\text{SbO}_4 + \text{NaCl} \longrightarrow \text{NaH}_2\text{SbO}_4 \downarrow + \text{KCl}$
White ppt.
- (iv) Mg^{2+} gives white ppt. of magnesium hydroxide with sodium hydroxide
 $\text{Mg}^{2+} + 2\text{NH}_3 + 2\text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2 \downarrow + 2\text{NH}_4^+$
 The ppt. obtained is sparingly soluble in water but readily soluble in ammonium salt.

Problem 1: An aqueous solution of gas (X) shows the following reactions :-

- (i) *It turns red litmus blue.*
 (ii) *When added in excess to a copper sulphate solution, a deep blue colour is obtained.*
 (iii) *On addition of FeCl_3 solution a brown ppt. soluble in dilute nitric acid is obtained.*
Identify (X) and give equations for the reactions at step (ii) & (iii)

Solution:

X - NH_3

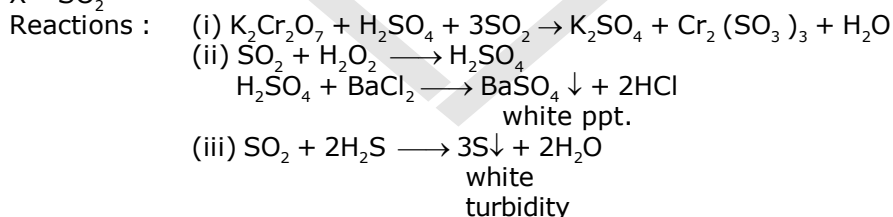


Problem 2: An aqueous solution of a gas (X) gives the following reactions:

- (i) *It decolourizes an acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution.*
 (ii) *On boiling with H_2O_2 , cooling it and then adding an aqueous solution of BaCl_2 , a white ppt. insoluble in dilute HCl is obtained.*
 (iii) *On passing H_2S into the solution, turbidity is obtained.*
Identify (X) and give equations for the steps (i), (ii), (iii) .

Solution:

X - SO_2



Problem 3: A white amorphous powder (A) on strongly heating gives a colourless non-combustible gas (B) and solid (C). The gas (B) turns lime water milky and turbidity disappears with the passage of excess of gas. The solution of (C) in dilute HCl gives a white ppt. with an aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$. The solution of (A) in dilute HCl gives a white ppt. (D) on passing H_2S in presence of excess of NH_4OH . Identify (A) to (D) by giving chemical equations.

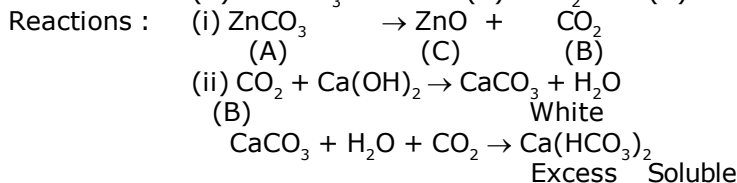
Solution:

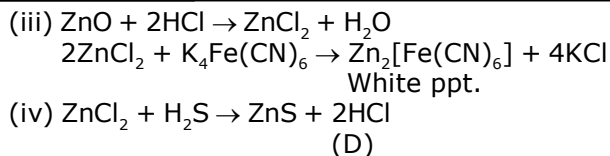
(A) - ZnCO_3

(B) - CO_2

(C) - ZnO

(D) - ZnS

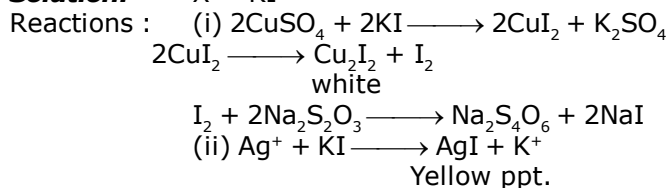




Problem 4: A certain compound (X) is used in laboratory for analysis. Its aq. solution gave the following reactions.

- (i) On addition to copper sulphate solution, a brown ppt. is obtained which turns white on addition of excess of $\text{Na}_2\text{S}_2\text{O}_3$ solution.
 (ii) On addition to Ag^+ ion solution, a yellow ppt. is obtained which is insoluble in NH_4OH . Identify (X), giving reactions

Solution: X - KI

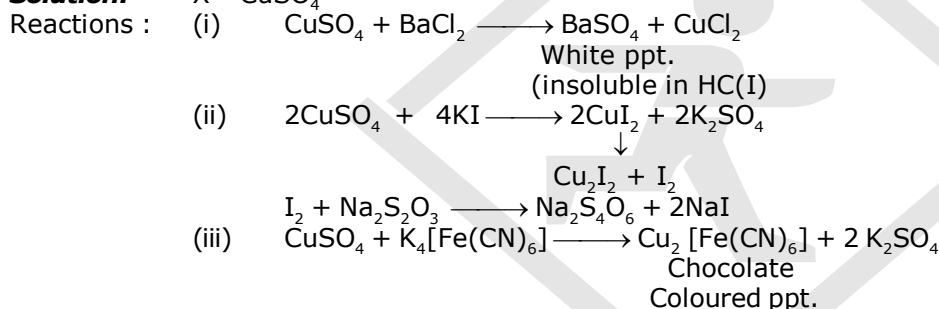


The white ppt. of Cu_2I_2 is coloured brown due to the presence of I_2 . On adding sodium thiosulphate, I_2 is consumed. Therefore the ppt. appears white.

Problem 5: An aqueous solution of inorganic compound (X) gives the following reactions:

- (i) With an aq. solution of barium chloride a ppt. insoluble in dil. HCl is obtained.
 (ii) Addition of excess of KI gives a brown ppt. which turns white on addition of excess of hypo.
 (iii) With an aqueous solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$ a chocolate coloured ppt. is obtained.
 Identify (X) and give equations for the reactions for (i), (ii) and (iii) observations.

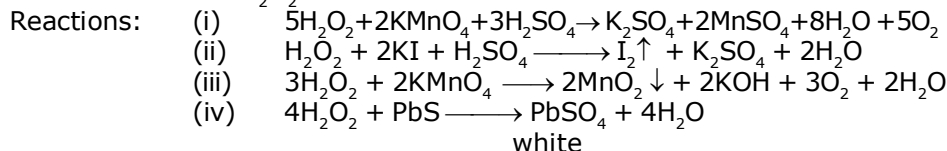
Solution: X - CuSO_4



Problem 6: An aq. solution of an inorganic compound (X) shows the following reactions.

- (i) It decolorizes an acidified KMnO_4 solution accompanied with evolution of O_2 .
 (ii) It liberates I_2 from acidified KI solution.
 (iii) It gives brown ppt. with alkaline KMnO_4 solution with evolution of O_2 .
 (iv) It is used to restore old oil paintings. Identify (X) and give chemical reactions for the steps (i) to (iv).

Solution: X - H_2O_2

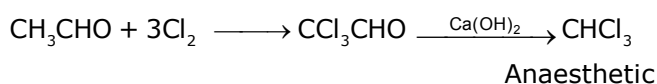
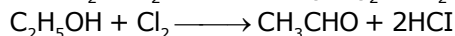
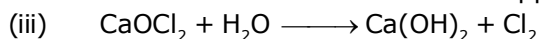
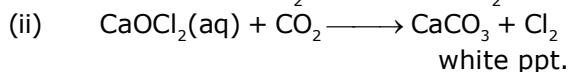
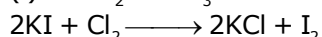


Problem 7: A certain compound (X) shows the following reactions :

- (i) When KI is added to an aq. suspension of (X) containing acetic acid, iodine is liberated
 (ii) When CO_2 is passed through an aq. suspension of (X) the turbidity transforms to a ppt.
 (iii) When a paste of (X) in water is heated with ethyl alcohol a product of anaesthetic use is obtained.

Identify (X) and write down chemical equations for reactions involved in steps (i), (ii) and (iii)

Solution: X - CaOCl_2



Problem 8: An inorganic Lewis acid (X) shows the following reactions :

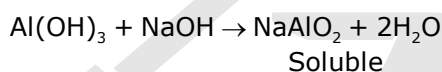
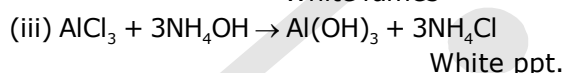
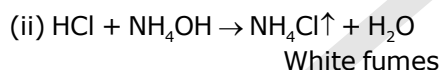
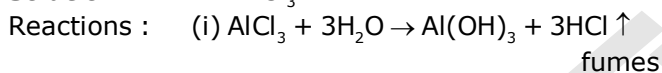
(i) It fumes in moist air.

(ii) The intensity of fumes increases when a rod dipped in NH_4OH is brought near it.

(iii) An acidic solution of (X) on addition of NH_4Cl and NH_4OH gives a precipitate which dissolves in NaOH solution.

(iv) An acidic solution of (X) does not give a precipitate with H_2S . Identify (X) and give chemical equation for steps (i) to (iii) .

Solution: X - AlCl_3



Problem 9: (i) A black mineral (A) on treatment with dilute sodium cyanide solution in presence of air gives a clear solution of (B) and (C).

(ii) The solution of (B) on reaction with zinc gives a precipitate of metal (D).

(iii) (D) is dissolved in dil. HNO_3 and the resulting solution gives a white precipitate (E) with dil. HCl .

(iv) (E) on fusion with sodium carbonate gives (D).

(v) (E) dissolves in aqueous solution of ammonia giving a colourless solution of (F). Identify (A) to (F) and give chemical equations for reactions involved in steps (i) to (v).

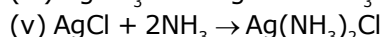
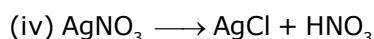
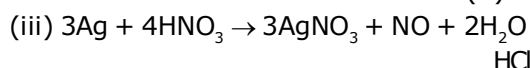
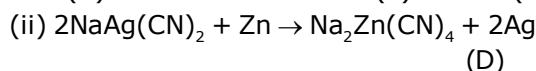
Solution: (A) - Ag_2S (B) - $\text{NaAg}(\text{CN})_2$

(C) - Na_2SO_4 (D) Ag

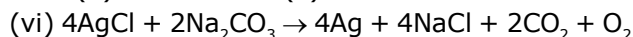
(E) AgCl (F) - $\text{Ag}(\text{NH}_3)_2\text{Cl}$



(A) (B) (C)



(E) (F)



(i) ***It imparts green colour to flame.***

(ii) **Its solution does not give ppt. on passing H_2S .**

(iii) When it is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 a red gas is evolved. The gas when passed in aq. NaOH solution turns it yellow. Identify (A) giving chemical reactions.

Solution: A - BaCl_2

Reactions : (i) $2\text{BaCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{CrO}_2\text{Cl}_2 + 2\text{BaSO}_4 + 3\text{H}_2\text{O}$
red gas

(ii) $\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}$
red gas
yellow
solution

Problem 11: NH_4SCN can be used to test one or more out of Fe^{3+} , Co^{2+} , Cu^{2+}

(A) Fe^{3+} only (B) Co^{2+} , Cu^{2+} (C) Fe^{3+} , Cu^{2+} (D) All

Solution: (D)

Problem 12: Ag_2S is soluble in NaCN due to formation of

(A) $\text{Na}[\text{Ag}(\text{CN})_2]$ (B) $\text{Ag}(\text{CN})_2$ (C) $\text{Na}_2\text{Ag}(\text{CN})_3$ (D) $\text{Na}_2[\text{Ag}(\text{CN})_2]$

Solution: (A)

Problem 13: *There is foul smell in presence of moisture with*

(A) $AlCl_3$ (B) $Al_2(SO_4)_3$ (C) FeS (D) $FeSO_4$

Solution: (C)

Problem 14: AgNO_3 on treatment with hypo gives white ppt. changing to black after some time. Black ppt. is

(A) $Ag_2S_2O_3$ (B) Ag_2SO_4 (C) $Ag_2S_4O_6$ (D) Ag_2S

Solution: (D)

Problem 15: Yellow coloured solution of FeCl_3 changes to light green when

(A) SnCl_2 is added (B) Zn is added
(C) H_2S gas is passed (D) Any one of the above is added.

Solution: (D)

Problem 16: $\text{Fe}(\text{OH})_3$ and $\text{Cr}(\text{OH})_3$ precipitate are separated by

(A) $[Ag(NH_3)_2]^+$ (B) HCl (C) $NaOH/H_2O_2$ (D) H_2SO_4

Solution: (C)

Problem 17: Evolution of deep red vapours when an inorganic salt is mixed with powdered $K_2Cr_2O_7$ and heated with conc. H_2SO_4 confirms the presence of a

(A) chloride (B) fluoride (C) borate (D) phosphate

Solution: (A)

Problem 18: Which of the following would enable you to remove SO_4^{2-} ions from a mixture of SO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$ and Cl^- ions?

(A) NaOH (B) KOH (C) $\text{Ba}(\text{OH})_2$ (D) BaSO_4

Solution: (C)

Problem 19: Which of the following sulphates is insoluble in water?

(A) CuSO_4 (B) CdSO_4 (C) PbSO_4 (D) $\text{Bi}(\text{SO}_4)_3$

Solution: (C)

Problem 20: A fire work gave bright crimson light. It probably contained a salt of

(A) Ca (B) Sr (C) Ba (D) Mg

Solution: (B)

EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. In the precipitation of the iron group in qualitative analysis, ammonium chloride is added before adding ammonium hydroxide to-
- (A) decrease concentration of OH^- ions.
 (B) prevent interference by phosphate ions
 (C) increase concentration of Cl^- ions.
 (D) increase concentration of NH_4^+ ions.

Sol.

2. A salt gives violet vapours when treated with conc. H_2SO_4 , it contains.
- (A) Cl^- (B) I^- (C) Br^- (D) NO_3^-

Sol.

3. The acidic solution of a salt produced a deep blue colour with starch iodide solution. The salt may be-
- (A) chloride (B) nitrite
 (C) acetate (D) bromide

Sol.

4. When a mixture of solid NaCl , solid $\text{K}_2\text{Cr}_2\text{O}_7$ is heated with conc. H_2SO_4 , orange red vapours are obtained. These are of the compound.
- (A) chromous chloride (B) chromyl chloride
 (C) chromic chloride (D) chromic sulphate

Sol.

5. Which of the following pairs of ions would be expected to form precipitate when dilute solution are mixed?

- (A) Na^+ , SO_4^{2-} (B) NH_4^+ , CO_3^{2-}
 (C) Na^+ , S_2^{2-} (D) Fe^{3+} , PO_4^{3-}

Sol.

6. Nessler's reagent is-

- (A) K_2HgI_4 (B) $\text{K}_2\text{HgI}_4 + \text{KOH}$
 (C) $\text{K}_2\text{HgI}_2 + \text{KOH}$ (D) $\text{K}_2\text{HgI}_4 + \text{KI}$

Sol.

7. When bismuth chloride is poured into a large volume of water the white precipitate produced is-
- (A) $\text{Bi}(\text{OH})_3$ (B) Bi_2O_3 (C) BiOCl (D) Bi_2OCl_3

Sol.

8. Ferric ion forms a prussian blue coloured ppt. of-

- (A) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (B) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
 (C) KMnO_4 (D) $\text{Fe}(\text{OH})_3$

Sol.

9. A mixture, on heating with conc. H_2SO_4 and MnO_2 , liberates brown vapour of-

- (A) Br_2 (B) NO_2 (C) HBr (D) I_2

Sol.

10. Which one of the following can be used in place of NH_4Cl for the identification of the third group radicals?

- (A) NH_4NO_3 (B) $(\text{NH}_4)_2\text{SO}_4$
 (C) $(\text{NH}_4)_2\text{S}$ (D) $(\text{NH}_4)_2\text{CO}_3$

Sol.

11. At the occasion of marriage, the fire works are used, which of the following gives green flame?

- (A) Ba (B) K (C) Be (D) Na

Sol.

12. Nitrate is confirmed by ring test. The brown colour of the ring is due to formation of-
- (A) ferrous nitrite (B) nitroso ferrous sulphate
(C) ferrous nitrate (D) FeSO_4NO_2

Sol.

13. $\text{Fe}(\text{OH})_3$ can be separated from $\text{Al}(\text{OH})_3$ by addition of-
- (A) dil. HCl (B) NaCl solution
(C) NaOH solution (D) NH_4Cl and NH_4OH

Sol.

14. If NaOH is added to an aqueous solution of zinc ions a white ppt appears and on adding excess NaOH, the ppt dissolves. In this solution zinc exist in the-
- (A) cationic part (B) anionic part
(C) both in cationic and anionic parts
(D) there is no zinc ion in the solution

Sol.

15. Mark the compound which is soluble in hot water.
- (A) Lead chloride (B) Mercurous chloride
(C) Strontium sulphate (D) Silver chloride

Sol.

16. Colour of nickel chloride solution is-
- (A) pink (B) black
(C) colourless (D) green

Sol.

17. Sometimes yellow turbidity appears while passing H_2S gas even in the absence of II group radicals. This is because of-
- (A) sulphur is present in the mixture as impurity
(B) IV group radicals are precipitated as sulphides.
(C) the oxidation of H_2S gas by some acid radicals.
(D) III group radicals are precipitated as hydroxides.

Sol.

18. The ion that cannot be precipitated by H_2S and HCl is-
- (A) Pb^{2+} (B) Cu^{2+} (C) Ag^+ (D) Ni^{2+}

Sol.

19. In V group, $(\text{NH}_4)_2\text{CO}_3$ is added to precipitate out the carbonates. We do not add Na_2CO_3 along with NH_4Cl because
- (A) CaCO_3 is soluble in Na_2CO_3
(B) Na_2CO_3 increase the solubility of V group carbonate.
(C) MgCO_3 will be precipitated out in V group
(D) None of these

Sol.

20. CuSO_4 decolourises on addition of excess KCN, the product is-
- (A) $[\text{Cu}(\text{CN})_4]^{2-}$
(B) Cu^{2+} get reduced to form $[\text{Cu}(\text{CN})_4]^{3-}$
(C) $\text{Cu}(\text{CN})_2$ (D) CuCN

Sol.

21. Which of the following cations is detected by the flame test ?
- (A) NH_4^+ (B) K^+ (C) Mg^{2+} (D) Al^{3+}

Sol.

22. Which one among the following pairs of ions cannot be separated by H_2S in dilute HCl?
- (A) Bi^{3+} , Sn^{4+} (B) Al^{3+} , Hg^{2+}
(C) Zn^{2+} , Cu^{2+} (D) Ni^{2+} , Cu^{2+}

Sol.

- 23.** A metal salt solution gives a yellow ppt with silver nitrate. The ppt dissolves in dil. nitric acid as well as in ammonium hydroxide. The solution contains
 (A) bromide (B) iodide
 (C) phosphate (D) chromate

Sol.

- 24.** A metal salt solution forms a yellow ppt with potassium chromate in acetic acid, a white ppt with dilute sulphuric acid, but gives no ppt with sodium chloride or iodide, it is:
 (A) lead carbonate (B) basic lead carbonate
 (C) barium nitrate (D) strontium nitrate

Sol.

- 25.** Which is soluble in NH_4OH ?
 (A) PbCl_2 (B) AgCl (C) PbSO_4 (D) CaCO_3

Sol.

- 26.** Which of the following combines with Fe(II) ions to form a brown complex
 (A) N_2O (B) NO (C) N_2O_3 (D) N_2O_4

Sol.

- 27.** Nessler's reagent is used to detect-
 (A) CrO_4^{2-} (B) PO_4^{3-} (C) MnO_4^- (D) NH_4^+

Sol.

- 28.** Prussian blue is formed when-
 (A) ferrous sulphate reacts with FeCl_3
 (B) ferric sulphate reacts with $\text{K}_4[\text{Fe(CN)}_6]$.
 (C) Ammonium sulphate reacts with FeCl_3
 (D) ferrous ammonium sulphate reacts with FeCl_3

Sol.

- 29.** What product is formed by mixing the solution of $\text{K}_4[\text{Fe(CN)}_6]$ with the solution of FeCl_3 ?
 (A) Ferro-ferricyanide (B) Ferri-ferrocyanide
 (C) Ferri-ferricyanide (D) None of these

Sol.

- 30.** Which of the following will not give positive chromyl chloride test ?
 (A) Copper chloride, CuCl_2
 (B) Mercuric chloride, HgCl_2
 (C) Zinc chloride, ZnCl_2
 (D) Anilinium chloride, $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$

Sol.

- 31.** A blue colouration is not obtained when-
 (A) ammonium hydroxide dissolves in copper sulphate.
 (B) copper sulphate solution reacts with $\text{K}_4[\text{Fe(CN)}_6]$
 (C) ferric chloride reacts with sodium ferrocyanide.
 (D) anhydrous white CuSO_4 is dissolved in water.

Sol.

- 32.** AgCl dissolves in ammonia solution giving.
 (A) Ag^+ , NH_4^+ and Cl^- (B) $\text{Ag}(\text{NH}_3)^+$ and Cl^-
 (C) $\text{Ag}_2(\text{NH}_3)^{2+}$ and Cl^- (D) $\text{Ag}(\text{NH}_3)_2^+$ and Cl^-

Sol.

- 33.** A white crystalline substance dissolves in water. On passing H_2S gas in this solution, a black ppt is obtained. The black ppt dissolves completely in hot HNO_3 . On adding a few drops of conc. H_2SO_4 , a white ppt is obtained. This ppt is that of-

- (A) BaSO_4 (B) SrSO_4
 (C) PbSO_4 (D) CdSO_4

Sol.

34. When excess of SnCl_2 is added to a solution of HgCl_2 , a white ppt turning grey is obtained. The grey colour is due to the formation of-
- (A) Hg_2Cl_2 (B) SnCl_4 (C) Sn (D) Hg

Sol.

35. Of the following sulphides which one is insoluble in dil. acids but soluble in alkalies.
- (A) PbS (B) CdS (C) FeS (D) As_2S_3

Sol.

36. When chlorine water is added to an aqueous solution of potassium halide in presence of chloroform, a violet colour is obtained. On adding more of chlorine water, the violet colour disappears, and a colourless solution is obtained. This test confirms the presence of the following in aqueous solution

(A) Iodide (B) Bromide
(C) Chloride (D) Iodide and bromide

Sol.

37. An aqueous solution of colourless metal sulphate M, gives a white ppt, with NH_4OH . This was soluble in excess of NH_4OH . On passing H_2S through this solution a white ppt is formed. The metal M in the salt is-

(A) Ca (B) Ba (C) Al (D) Zn

Sol.

38. When AgNO_3 is strongly heated, the products formed are-

(A) NO and NO_2 (B) NO_2 and O_2
(C) NO_2 and N_2O (D) NO and O_2

Sol.

39. AgCl is soluble in-

(A) Aqua regia (B) H_2SO_4
(C) dil. HCl (D) aq. NH_3

Sol.

40. A substance on treatment with dil. H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of-

(A) CO_3^{2-} (B) S^{2-} (C) SO_3^{2-} (D) NO_2^-

Sol.

41. When copper nitrate is strongly heated, it is converted into-

(A) Cu metal (B) cupric oxide
(C) cuprous oxide (D) copper nitrate

Sol.

42. A white solid is first heated with dil H_2SO_4 and then with conc. H_2SO_4 . No action was observed in either case. The solid salt contains-

(A) sulphide (B) sulphite
(C) thiosulphate (D) sulphate

Sol.

43. A pale green crystalline metal salt of M dissolves freely in water. On standing it gives a brown ppt on addition of aqueous NaOH. The metal salt solution also gives a black ppt on bubbling H_2S in basic medium. An aqueous solution of the metal salt decolourizes the pink colour of the permanganate solution. The metal in the metal salt solution is-

(A) copper (B) aluminium (C) lead (D) iron

Sol.

- 44.** On the addition of a solution containing CO_4^{2-} ions to the solution of Ba^{2+} , Sr^{2+} and Ca^{2+} ions, the ppt obtained first will be of-
- (A) CaCO_4 (B) SrCrO_4
 (C) BaCrO_4
 (D) a mixture of all the three

Sol.

- 45.** Turnbull's blue is a compound-
- (A) ferricyanide (B) ferro ferricyanide
 (C) ferrous cyanide (D) ferri ferrocyanide

Sol.

- 46.** Sodium borate on reaction with conc. H_2SO_4 and $\text{C}_2\text{H}_5\text{OH}$ gives a compound A which burns with a green edged flame. The compound A is-
- (A) $\text{H}_2\text{B}_4\text{O}_7$ (B) $(\text{C}_2\text{H}_5)_2\text{B}_4\text{O}_7$
 (C) H_3BO_3 (D) $(\text{C}_2\text{H}_5)_3\text{BO}_3$

Sol.

- 47.** When $\text{K}_2\text{Cr}_2\text{O}_7$ crystals are heated with conc. HCl , the gas evolved is-
- (A) O_2 (B) Cl_2 (C) CrO_2Cl_2 (D) HCl

Sol.

- 48.** Which is most soluble in water ?
- (A) AgCl (B) AgBr (C) AgI (D) AgF

Sol.

- 49.** On passing H_2S gas in II group sometimes the solution turns milky. It indicates the presence of-
- (A) oxidising agent (B) acidic salt
 (C) thiosulphate (D) reducing agent

Sol.

- 50.** Dimethyl glyoxime in a suitable solvent was refluxed for 10 minutes with pure pieces of nickel sheet, it will result in-
- (A) Red ppt (B) Blue ppt.
 (C) Yellow ppt. (D) No ppt.

Sol.

- 51.** A mixture of chlorides of copper, cadmium, chromium, iron and aluminium was dissolved in water acidified with HCl and hydrogen sulphide was passed for sufficient time. It was filtered, boiled and a few drops of nitric acid were added while boiling. To this solution ammonium chloride and sodium hydroxide were added in excess and filtrate shall give test for-
- (A) sodium and iron ion
 (B) sodium, chromium and aluminium ion
 (C) aluminium and iron ion
 (D) sodium, iron, cadmium and aluminium ion

Sol.

- 52.** A metal is burnt in air and the ash on moistening smells of ammonia. The metal is-
- (A) Na (B) Fe (C) Mg (D) Al

Sol.

53. Solution of chemical compound X reacts with AgNO_3 solution to form a white ppt. Y which dissolves in NH_4OH to give a complex Z. When Z is treated with dil. HNO_3 , Y reappears. The chemical compound X can be-

- (A) NaCl (B) CH_3Cl (C) NaBr (D) NaI

Sol.

54. A white ppt obtained in a analysis of a mixture becomes black on treatment with NH_4OH . It may be-

- (A) PbCl_2 (B) AgCl (C) HgCl_2 (D) Hg_2Cl_2

Sol.

55. A salt on treatment with dil. HCl gives a pungent smelling gas and a yellow precipitate. The salt gives green flame when tested. The solution gives a yellow precipitate with potassium chromate. The salt is :

- (A) NiSO_4 (B) BaS_2O_3
(C) PbS_2O_3 (D) CuSO_4

Sol.

56. Which compound does not dissolve in hot dilute HNO_3 ?

- (A) HgS (B) PbS (C) CuS (D) CdS

Sol.

57. An aqueous solution of FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are :

- (A) a colourless filtrate and a green residue
(B) a yellow filtrate and a green residue
(C) a yellow filtrate and a brown residue
(D) a green filtrate and a brown residue

Sol.

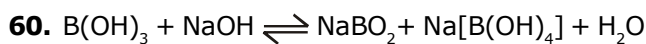
58. Which of the following compound on reaction with NaOH and Na_2O_2 gives yellow colour?

- (A) $\text{Cr}(\text{OH})_3$ (B) $\text{Zn}(\text{OH})_2$
(C) $\text{Al}(\text{OH})_3$ (D) None of these

Sol.

59. CrO_3 dissolves in aqueous NaOH to give :

- (A) $\text{Cr}_2\text{O}_7^{2-}$ (B) CrO_4^{2-}
(C) $\text{Cr}(\text{OH})_3$ (D) $\text{Cr}(\text{OH})_2$

Sol.

How can this reaction is made to proceed in forward direction ?

- (A) addition of cis 1,2 diol
- (B) addition of borax
- (C) addition of trans 1,2 diol
- (D) addition of Na_2HPO_4

Sol.

61. Statement-1 : On passing CO_2 gas through lime water, the solution turns milky.

because

Statement-2 Acid Base (neutralisation) reaction takes place.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

Sol.

62. An aqueous solution of a substance gives a white ppt. on treatment with dil. HCl , which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black ppt. is obtained. The substance is a-

- (A) Hg^{2+} salt
- (B) Cu^{2+} salt
- (C) Ag^+ salt
- (D) Pb^{2+} salt

Sol.

63. Which of the following does not produce metallic sulphide with H_2S ?

- (A) ZnCl_2
- (B) CdCl_2
- (C) CoCl_2
- (D) FeCl_2

Sol.

64. A pale yellow crystalline solid insoluble in water but soluble in CS_2 is allowed to react with nitric oxide to give X and Y. X is a colourless gas with pungent odour. X is further allowed to react in aqueous medium with nitric oxide to yield Z and T. Compounds X, Z and T are-

- (A) $\text{SO}_3, \text{H}_2\text{SO}_3$
- (B) $\text{SO}_2, \text{H}_2\text{SO}_4, \text{N}_2\text{O}$
- (C) $\text{SiO}_2, \text{H}_2\text{SO}_4, \text{N}_2$
- (D) $\text{SO}_3, \text{H}_2\text{SO}_3, \text{N}_2$

Sol.

65. Which metal salt gives a violet coloured bead in the borax bead test ?

- (A) Fe^{2+} (B) Ni^{2+} (C) Co^{2+} (D) Mn^{2+}

Sol.

66. Which of the following gives a precipitate with $\text{Pb}(\text{NO}_3)_2$ but no with $\text{Ba}(\text{NO}_3)_2$?

- (A) Sodium chloride
(B) Sodium acetate
(C) Sodium nitrate
(D) Sodium hydrogen phosphate

Sol.

67. Which of the following is soluble in yellow ammonium sulphide ?

- (A) CuS (B) CdS (C) SnS (D) PbS

Sol.

68. A chloride dissolves appreciable in cold water. When placed on a platinum wire in Bunsen flame to distinctive colour is noticed, the cation would be :

- (A) Mg^{2+} (B) Ba^{2+} (C) Pb^{2+} (D) Ca^{2+}

Sol.

69. A white salt is readily soluble in water and gives a colourless solution with a pH of about 9. The salt could be-

- (A) NH_4NO_3 (B) CH_3COONa
(C) $\text{CH}_3\text{COONH}_4$ (D) CaCO_3

Sol.

70. An element (X) forms compounds of the formula XCl_3 , X_2O_5 and Ca_3X_2 , but does not form XCl_5 . Which of the following is the element X ?

- (A) B (B) Al (C) N (D) P

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil. HNO_3 . The anion could be :

(A) CO_3^{2-} (B) Cl^- (C) SO_4^{2-} (D) S^{2-}

Sol.

2. A mixture of two salts is not water soluble but dissolves completely in dil HCl to form a colourless solution. The mixture could be :

(A) AgNO_3 and KBr (B) BaCO_3 and ZnS
(C) FeCl_5 and CaCO_3 (D) $\text{Mn(NO}_3)_2$ and MgSO_4

Sol.

3. Three separate samples of a solution of a single salt gave these results. One formed a white precipitate with excess of ammonia solution, one formed a white precipitate with dil NaCl solution and one formed a black precipitate with H_2S . The salt could be :

(A) AgNO_3 (B) $\text{Pb(NO}_3)_2$
(C) $\text{Hg(NO}_3)_2$ (D) MnSO_4

Sol.

4. Which one of the following ionic species will impart colour to an aqueous solution ?

(A) Ti^{4+} (B) Cu^+ (C) Zn^{2+} (D) Cr^{3+}

Sol.

5. When a substance A reacts with water it produces a combustible gas B and a solution of substance C in water. When another substance D reacts with this solution of C, it also produces the same gas B on warming but D can produce gas B on reaction with dilute sulphuric acid at room temperature. A imparts a deep golden yellow colour a smokeless flame to Bunsen burner. A, B, C and D respectively are :

(A) $\text{Na}, \text{H}_2, \text{NaOH}, \text{Zn}$
(B) $\text{K}, \text{H}_2, \text{KOH}, \text{Al}$
(C) $\text{Ca}, \text{H}_2, \text{Ca(OH)}_2, \text{Sn}$
(D) $\text{CaC}_2, \text{C}_2\text{H}_2, \text{Ca(OH)}_2, \text{Fe}$

Sol.

6. Which is not dissolved by dil HCl ?

(A) ZnS (B) MnS (C) BaSO_3 (D) BaSO_4

Sol.

7. The brown ring test for NO_2^- and NO_3^- is due to the formation of complex ion with formula :

(A) $[\text{Fe(H}_2\text{O)}_6]^{2+}$ (B) $[\text{Fe(NO)(CN)}_5]^{2-}$
(C) $[\text{Fe(H}_2\text{O)}_5(\text{NO})]^{2+}$ (D) $[\text{Fe(H}_2\text{O)(NO)}_5]^{2+}$

Sol.

8. In Nessler's reagents, the ion present is :

(A) HgI_2^{2-} (B) HgI_4^{2-} (C) Hg^+ (D) Hg^{2+}

Sol.

9. The cations present in slightly acidic solution are Fe^{3+} , Zn^{2+} and Cu^{2+} . The reagent which when added in excess to this solution would identify and separate Fe^{3+} in one step is :

(A) 2 M HCl (B) 6 M NH_3
(C) 6 M NaOH (D) H_2S gas

Sol.

10. Which of the following leaves no residue on heating ?

- (A) $\text{Pb}(\text{NO}_3)_2$ (B) NH_4NO_3
(C) $\text{Cu}(\text{NO}_3)_2$ (D) NaNO_3

Sol.

11. When I_2 is passed through KCl , KF , KBr :

- (A) Cl_2 and Br_2 are evolved
(B) Cl_2 is evolved
(C) Cl_2 , F_2 and Br_2 are evolved
(D) None of these

Sol.

12. In the separation of Cu^{2+} and Cd^{2+} in 2nd group qualitative analysis of cations tetrammine copper (II) sulphate and tetrammine cadmium (II) sulphate react with KCN to form the corresponding cyano complexes. Which one of the following pairs of the complexes and their relative stability enables the separation of Cu^{2+} and Cd^{2+} ?

- (A) $\text{K}_3[\text{Cu}(\text{CN})_4]$ more stable and $\text{K}_2[\text{Cd}(\text{CN})_4]$ less stable
(B) $\text{K}_2[\text{Cu}(\text{CN})_4]$ less stable and $\text{K}_2[\text{Cd}(\text{CN})_4]$ more stable
(C) $\text{K}_2[\text{Cu}(\text{CN})_4]$ more stable and $\text{K}_2[\text{Cd}(\text{CN})_4]$ less stable.
(D) $\text{K}_3[\text{Cu}(\text{CN})_4]$ less stable and $\text{K}_2[\text{Cd}(\text{CN})_4]$ more stable.

Sol.

13. Which one has the minimum solubility product ?

- (A) AgCl (B) AlCl_3 (C) BaCl_2 (D) NH_4Cl

Sol.

14. Which of the following sulphate is insoluble in water ?

- (A) CuSO_4 (B) CdSO_4
(C) PbSO_4 (D) $\text{Bi}_2(\text{SO}_4)_3$

Sol.

15. A metal X on heating in nitrogen gas gives Y.Y. on treatment with H_2O gives a colourless gas which when passed through CuSO_4 solution gives a blue colour Y is :

- (A) $\text{Mg}(\text{NO}_3)_2$ (B) Mg_3N_2 (C) NH_3 (D) MgO

Sol.

16. Which of the following gives blood red colour with KCNS ?

- (A) Cu^{2+} (B) Fe^{3+} (C) Al^{3+} (D) Zn^{2+}

Sol.

17. Which of the following is insoluble in excess of NaOH ?

- (A) $\text{Al}(\text{OH})_3$ (B) $\text{Cr}(\text{OH})_3$
(C) $\text{Fe}(\text{OH})_3$ (D) $\text{Zn}(\text{OH})_2$

Sol.

18. In the borax bead test of Co^{2+} , the blue colour of bead is due to the formation of

- (A) B_2O_3 (B) Co_3B_2
(C) $\text{Co}(\text{BO}_2)_2$ (D) CoO

Sol.

19. Mercurous ion is represented as :

- (A) Hg_2^{2+} (B) Hg^{2+} (C) $\text{Hg} + \text{Hg}^{2+}$ (D) Hg_2^+

Sol.

20. The metal ion which is precipitated when H_2S is passed with HCl :

- (A) Zn^{2+} (B) Ni^{2+} (C) Cd^{2+} (D) Mn^{2+}

Sol.

21. Which of the following is not a preliminary test used to detect ions :

- (A) borax bead test (B) flame test
(C) brown ring test (D) cobalt nitrate test

Sol.

22. Which one of the following metal sulphides has maximum solubility in water ?

- (A) HgS , $K_{sp} = 10^{-54}$ (B) CdS , $K_{sp} = 10^{-30}$
(C) FeS , $K_{sp} = 10^{-20}$ (D) ZnS , $K_{sp} = 10^{-22}$

Sol.

23. The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is :

- (A) Cu (B) CuBO_2
(C) $\text{Cu}(\text{BO}_2)_2$ (D) None of these

Sol.

24. Statement-1 : NO_2^- ion can not be detected by brown ring test in presence of NO_3^- ion.

Statement-2 : Both NO_2^- and NO_3^- ions are confirmed by brown ring test.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

Sol.

25. Read of the following statements and choose the correct code w.r.t. true(T) and false (F).

- (I) manganese salts give a violet borax bead test in reducing flame
(II) from a mixed precipitate of AgCl and AgI , ammonia solution dissolves only AgCl
(III) ferric ions give a deep green precipitate, on adding potassium ferrocyanide solution
(IV) on boiling the solution having K^+ , Ca^{2+} and HCO_3^- we get a precipitate of $\text{K}_2\text{Ca}(\text{CO}_3)_2$
(A) TTFF (B) FTFT (C) FTFF (D) TTFT

Sol.

26. Identify the correct order of solubility of Na_2S , CuS and ZnS in aqueous medium is :

- (A) $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$ (B) $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$
(C) $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$ (D) $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$

Sol.

27. When H_2S gas is passed through the HCl containing aqueous solution of CuCl_2 , HgCl_2 , BiCl_3 and CoCl_2 , it does not precipitate out :

- (A) CuS (B) HgS (C) Bi_2S_3 (D) CoS

Sol.

28. Mark the correct statement :

- (A) I group basic radicals precipitate as chlorides
 (B) IV group basic radicals precipitates as sulphides.
 (C) V group basic radicals precipitates as carbonates.
 (D) All the above statement are correct.

Sol.

29. Potassium chromate solution is added to an aqueous solution of a metal chloride. The precipitate thus obtained are insoluble in acetic acid. These are subjected to flame test, the colour of the flame is :

- (A) Lilac (B) Apple green
 (C) Crimson red (D) Golden yellow

Sol.

30. MgSO_4 on reaction with NH_4OH and Na_2HPO_4 forms a white crystalline precipitate. What is its formula?

- (A) $\text{Mg}(\text{NH}_4)\text{PO}_4$ (B) $\text{Mg}_3(\text{PO}_4)_2$
 (C) $\text{MgCl}_2 \cdot \text{MgSO}_4$ (D) MgSO_4

Sol.

COMPREHENSION

Q. NO. 31 to 33 (3 questions)

Compound 'A' $\xrightarrow{\Delta}$ Initially swelled

$\xrightarrow[\text{strong heating}]{\Delta}$ Amorphous powder

\searrow Lilac flame in the flame test.

Compound 'A' $\xrightarrow{\text{excess NaOH}}$ 'B' (No change in colour) $\xrightarrow{\text{H}_2\text{O}_2}$ 'C' (Yellow solution)

31. Compound 'A' is having water of crystallization by the number of -

- (A) 10 (B) 20 (C) 24 (D) 36

Sol.

32. The compound 'B' is having oxidation state of-

- (A) zero (B) II (C) III (D) IV

Sol.

33. The hybridization of compound 'C' is -

- (A) sp^3 (B) sp^3d (C) d^2sp^3 (D) d^3s

Sol.

Q. NO. 34 to 36 (3 questions)

A green ore (A) of a metal present as a double /mixed compound is treated with HCl and then H_2S is passed in the solution. A black precipitate (B) is obtained, that is insoluble in yellow ammonium sulphide. The precipitate is dissolved in HNO_3 and then excess of NH_4OH is added. The solution becomes coloured but this colour is discharged upon addition of KCN in excess due to the formation of compound (C). The solution of (A) in H_2O liberates a colourless and odourless gas on reaction with dilute H_2SO_4 and solution of (A) gives white precipitate on addition of $BaCl_2$ solution.

34. The green ore (A) is ?

- (A) $CuSO_4 \cdot Cu(OH)_2$ (B) $PbCO_3 \cdot Pb(OH)_2$
(C) $PbSO_4 \cdot Pb(OH)_2$ (D) $CuCO_3 \cdot Cu(OH)_2$

Sol.

35. After dissolving the precipitate in HNO_3 aqueous $K_4[Fe(CN)_6]$ is added and a precipitate is formed. (A) It is a reddish brown precipitate of $Cu_2[Fe(CN)_6]$.

(B) It is a reddish brown precipitate of $K_2Cu_3[Fe(CN)_6]_2$

(C) It is a chocolate brown precipitate of $Cu_2[Fe(CN)_6]$.

(D) It is a chocolate brown precipitate of $K_2Cu_3[Fe(CN)_6]_2$

Sol.

36. The procedure used to estimate the metal ion of ore (A) gravimetrically, is ?

- (A) Treatment of ore with excess KCN
(B) Treatment of solution of ore with Ag metal.
(C) Treatment of ore with excess ammonia
(D) Treatment of ore with excess KSCN.

Sol.

MATCH THE COLUMN :**37. Column-I**

- (A) Amphoteric metal oxide
(B) Metal acetate $\xrightarrow{\Delta}$ acetone + metal carbonate
(C) Metal acetate $\xrightarrow{\Delta}$ metal oxide + $CO_2 \uparrow$ + acetone
(D) Metal nitrate $\xrightarrow{\Delta}$ metal oxide + $NO_2 \uparrow$ + $O_2 \uparrow$

Column-II

- (P) Pb
(Q) Zn
(R) Na
(S) Li

Sol.

38. Which of anions in the Column-I shows one or more observations from the column-II.

Column-I

- (A) S^{2-}
(B) NO_2^-
(C) SO_3^{2-}
(D) CH_3COO^-

Column-II

- (P) White ppt. with $AgNO_3$
(Q) Evolution of pungent smell gas with
(R) Brown fumes with conc. H_2SO_4 (hot)
(S) Decolourises acidified $KMnO_4$

Sol.

EXERCISE – III**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Which one of the following does not react with AgCl ?

(A) ZnCl_2 (B) CdCl_2 (C) CoCl_2 (D) CuCl_2

Sol.

2. $\begin{array}{c} \text{A} \\ \text{(Mixture of two anion)} \end{array} \xrightarrow[\text{BaCl}_2]{\text{Cold}} \text{White ppt.} \xrightarrow{\text{Filtered}} \text{Blue}$
 $\text{litmus turns red} \xleftarrow{\text{H}_2\text{O}_2} \text{Filtrate}$

Mixture of A contain:

- (A) CO_3^{2-} , HCO_3^- anions
 (B) CO_3^{2-} , HSO_3^- anions
 (C) SO_3^{2-} , HSO_3^- anions
 (D) None of these

Sol.

3. The ions which can be precipitated with both HCl and H_2S are

(A) Pb^{2+} (B) Cu^{2+} (C) Ag^+ (D) Sn^{2+}

Sol.

4. When dimethyl glyxime solution is added to an aqueous solution of nickel (II) chloride followed by ammonium hydroxide then which of the following statements are incorrect?

- (A) No precipitate is obtained
 (B) A blue coloured ppt. is obtained
 (C) A rosy red coloured ppt. is obtained
 (D) A black coloured ppt. is obtained

Sol.

5. The brown ring test is performed for the qualitative detection of:

(A) Bromides (B) iodides
 (C) nitrates (D) nitrite

Sol.

6. Which of the following statement(s) is/are incorrect?

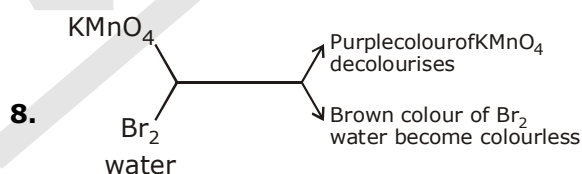
- (A) Manganese salts give a violet borax bead test in reducing flame
 (B) From a mixed precipitate of AgCl and AgI, ammonia solution dissolves only AgCl
 (C) Ferric ions give a deep green precipitate, on adding potassium ferrocyanide solution
 (D) On boiling the solution having K^+ , Ca^{2+} and HCO_3^- ions we get a precipitate of $\text{K}_2\text{Ca}(\text{CO}_3)_2$

Sol.

7. S^{2-} and SO_3^{2-} can be distinguished by using:

(A) $(\text{CH}_3\text{COO})_2\text{Pb}$ (B) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
 (C) $\text{Cr}_2\text{O}_7^{2-}$ (D) CaCl_2

Sol.



The gas will be :

(A) CO_2 (B) SO_2 (C) H_2S (D) SO_3

Sol.

Subjective

1.

- (i) An inorganic compound (A) is formed on passing a gas (B) through a conc. liquor containing Na_2S and sodium sulphite.
 (ii) On adding (A) into a dilute solution of silver nitrate a white precipitate appears which quickly changes into a black coloured compound. (C)

- (iii) On adding two or three drops of FeCl_3 into the excess of solution (A) a violet coloured compound (D) is formed. This colour disappears quickly.
- (iv) On adding a solution of (A) into the solution of cupric chloride, a white precipitate is first formed which dissolves on adding excess of (A) forming a compound (E).

Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (iv).

Sol.

2.

- (i) A black coloured compound (B) is formed on passing H_2S through the solution of a compound (A) in NH_4OH .
- (ii) (B) on treatment with HCl and potassium chlorate gives (A).
- (iii) (A) on treatment with KCN gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).
- (iv) The compound (C) is changed into a compound (D) when its aqueous solution is boiled.
- (v) The solution of (A) was treated with excess of NaHCO_3 & then with bromine water. On cooling & shaking for some time, a green colour of compound (E) is formed. No changes is observed on heating. Identify (A) to (E) and give chemical equations.

Sol.

3.

- (i) A blue coloured compound (A) on heating gives two of the products (B) & (C).
- (ii) A metal (D) is deposited on passing hydrogen through heated (B).
- (iii) The solution of (B) in HCl on treatment with the $\text{K}_4[\text{Fe}(\text{CN})_6]$ gives a chocolate brown coloured precipitate of compound (E).
- (iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound

(F). Identify (A) to (F) and give chemical equations for the reactions at step (i) to (iv).

Sol.

4.

- (i) An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds, (B) and (C).
- (ii) The solution of (B) in conc. HCl on treatment with potassium ferrocyanide gives a blue colour or precipitate of compound (D).
- (iii) The aqueous solution of (C) on treatment with conc. H_2SO_4 gives a orange coloured compound (E).
- (iv) Compound (E) when treated with KCl gives an orange red compound (F) which is used as an oxidising reagents.
- (v) The solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G). Identify (A) to (G) and give balanced chemical equations for reactions for reactions at step. (i) to (v).

Sol.

5. Complete the following by identifying (A) to (F).

- (i) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} (\text{A}) \xrightarrow{230^\circ\text{C}} (\text{B}) \xrightarrow{800^\circ\text{C}} (\text{C}) + (\text{D})$
- (ii) $\text{AgNO}_3 \xrightarrow{\text{Red hot}} (\text{E}) + (\text{F}) + \text{O}_2$

Sol.

EXERCISE – IV**PREVIOUS YEARS****LEVEL – I****JEE MAIN**

Q.1 HgCl_2 on passing H_2S gives - [AIEEE-2002]

- (A) HgS (B) Hg_2S
(C) $\text{Hg} + \text{HgS}$ (D) $\text{HgS} + \text{H}_2\text{S}$

Sol.

Q.3 Which statement is correct : [AIEEE-2003]

- (A) Fe^{3+} ions give deep green precipitate with $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution
(B) On heating K^+ , Ca^{2+} and HCO_3^- ions, we get a precipitate of $\text{K}_2[\text{Ca}(\text{CO}_3)_2]$
(C) Manganese salts give a violet borax bead test in the reducing flame
(D) From a mixed precipitate of AgCl and AgI ammonia solution dissolves only AgCl

Sol.

Q.2 How do we differentiate between Fe^{3+} and Cr^{3+} in qualitative analysis gp. III :

[AIEEE-2002]

- (A) By taking excess of NH_4OH
(B) By increasing NH_4^+ ion concentration
(C) By decreasing OH^- ion concentration
(D) Both (B) and (C)

Sol.

LEVEL – II

JEE ADVANCED

1. A compound (A) is greenish crystalline salt, which gave the following results.
- Addition of BaCl_2 solution to the solution of (A) results in the formation of white precipitate (B), which is insoluble in dil HCl.
 - On heating (A), water vapours and two oxides of sulphur (C) & (D) are liberated leaving a red brown residue (E).
 - (E) dissolves in warm concentrated HCl to give a yellow solution (F).
 - With H_2S the solution (F) yields a pale yellow precipitate (G) which when filtered, leaves a greenish filtrate (H).
 - Solution (F) with treatment of thiocyanate ion gives blood red coloured compound (I). Identify the substances from (A) to (D).

Sol.

2. A scarlet compound 'A' is treated with concentrated HNO_3 to give a chocolate brown precipitate 'B'. The precipitate is filtered and the filtrate is neutralised with NaOH. Addition of KI to the resulting solution gives a yellow precipitate 'C'. The precipitate B on warming with concentrated HNO_3 in the presence of $\text{Mn}(\text{NO}_3)_2$ produces a pink coloured solution due to the formation of 'D'. Identify 'A', 'B', 'C' & 'D'. Write the reaction sequence.

[JEE 1995]

Sol.

3. Calcium burns in nitrogen to produce a white powder which dissolves in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compound (A) and (B).

[JEE 1996]

Sol.

4. Gradual addition of KI solution to $\text{Bi}(\text{NO}_3)_3$ solution initially produces a dark brown precipitate which dissolves in excess of KI to give a clear yellow solution. Write equations for the above reactions.

[JEE 1996]

Sol.

5. A colourless inorganic salt [A] decomposes completely at about 250°C to give only two products, (B) and (C) leaving no residue. The oxide (C) is a liquid at room temperature and neutral to moist litmus paper while the gas (B) is neutral oxide. White phosphorus burns in excess of (B) to produce a strong white dehydrating agent. Write balanced equations for the following reactions involved in the above process.

[JEE 1996]

Sol.

6.

- (i) An aqueous solution of white coloured compound (A) on reaction with HCl gives a white precipitate of compound (B).
- (ii) (B) becomes soluble in chlorine water with formation of (C).
- (iii) (C) reacts with KI to give a precipitate which becomes soluble in excess of it forming a compound (D). Compound (D) is used for detecting ammonium salt.
- (iv) (B) and (C) both on treatment with SnCl_2 give a grey precipitate of (E).
- (v) When conc. H_2SO_4 is added slowly into a mixture of cold solution of (A) and FeSO_4 a brown ring of compound (F) is formed. Identify (A) to (F).

[JEE 1997]

Sol.

7. An aqueous blue coloured solution of a transition metal sulphate reacts with H_2S in acidic medium to give a black precipitate (A) which is insoluble in warm aqueous solution of KOH. The blue solution on treatment with KI in weakly acidic medium turns yellow and produces a white precipitate (B). Identify the transition metal ion. Write the chemical reactions involved in the formation of (A) and (B).

[JEE 2000]

Sol.

8.

- (i) A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B).
- (ii) The solution of (B) in boiling water on acidification with dilute H_2SO_4 gives a pink coloured compound (C).
- (iii) The aqueous solution of (A) on treatment with NaOH an Br_2 -water gives a compound (D).

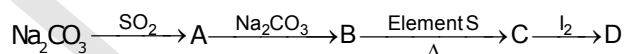
- (iv) A solution of (D) in conc. HNO_3 on treatment with lead peroxide at boiling temperature produced a compound (E) which was of the same colour as that of (C).
- (v) A solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of compound (F) which was insoluble in conc. HNO_3 and conc. HCl.

Identify (A) to (F) and give balanced chemical equations for the reactions at steps (i) to (v).

[JEE 2001]

Sol.

9. Identify the following :



Also mention the oxidation state of S in all the compounds.

[JEE 2002]

Sol.

10. A mixture consists A (yellow solid) and B (colourless solid) which gives lilac colour in flame.

- (a) Mixture gives black precipitate C on passing H_2S (g).
- (b) C is soluble in aqua-regia and on evaporation of aqua-regia and adding SnCl_2 gives greyish black precipitate D.

The salt solution with NH_4OH gives a brown precipitate.

- (i) The sodium extract of the salt with $\text{CCl}_4/\text{FeCl}_3$ gives a violet layer.
- (ii) The sodium extract gives yellow precipitate with AgNO_3 solution which is insoluble in NH_3 .

Identify A and B, and the precipitates C and D.

[JEE 2003]

Sol.

11. Dimethyl glyoxime is added to alcoholic solution of NiCl_2 . When ammonium hydroxide is slowly added to it a rosy red precipitate of a complex appears.

- Give the structure of complex showing hydrogen bonds.
- Give oxidation state and hybridization of central metal ion.
- Identify whether it is paramagnetic or diamagnetic

[JEE 2004]

Sol.

12. There are two ores (A_1) and (A_2) of metal (M). When ore (A_1) is calcinated a black solid (S) is obtained along with the liberation of CO_2 and water. The ore (A_1) on treatment with HCl and KI gives a precipitate (P) and iodine is liberated. Another ore (A_2) on roasting gives a gas (G) and metal (M) is set free. When gas (G) is passed through $\text{K}_2\text{Cr}_2\text{O}_7$ it turns green. Identify (M), (A_1), (A_2), (S), (P) and (G).

[JEE 004]

Sol.

13.



Identify A and B

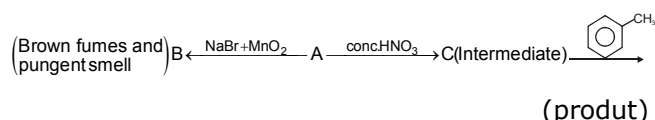
(a) Write IUPAC name of A and B

(b) Find out spin only magnetic moment of (b)

[JEE 2005]

Sol.

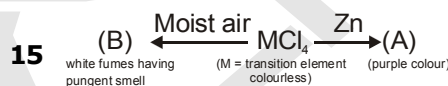
14.



Find A, B, C and D. Also write equations A to B and A to C.

[JEE 2005]

Sol.



Identify the metal M and hence MCl_4 . Explain the difference in colours of MCl_4 and A. [JEE 2005]

Sol.

16. In nitroprusside ion the iron and NO exist. No exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be differentiated by :

[JEE 1998]

- estimating the concentration of iron
- measuring the concentration of CN
- measuring the solid state magnetic moment
- thermally decomposing the compound

Sol.

17. Assertion : Sulphate is estimated as BaSO_4 and not as MgSO_4 . [JEE 1998]

Reason : Ionic radius of Mg^{2+} is smaller than that of Ba^{2+} .

(A) Both assertion and reason are correct, and reason is the correct explanation of the assertion
(B) Both assertion and reason are correct, but reason is not the correct explanation of the assertion.

(C) Assertion is correct but reason is incorrect.

(D) Assertion is incorrect but reason is correct.

Sol.

18. Which of the following statement (s) is (are) correct with reference to the ferrous and ferric ions

(A) Fe^{3+} gives brown colour with potassium ferricyanide [JEE 1998]

(B) Fe^{2+} gives blue precipitate with potassium ferricyanide

(C) Fe^{3+} give red colour with potassium thiocyanate

(D) Fe^{2+} gives brown colour with ammonium thiocyanate

Sol.

19. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a : [JEE 2000]

(A) Hg_2^{+} salt

(B) Cr^{2+} salt

(C) Ag^{+} salt

(D) Pb^{2+} salt

Sol.

20. A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white precipitate. the saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y': [JEE 2002(Mains)]

(A) $\text{X} = \text{CO}_2$, $\text{Y} = \text{Cl}_2$

(B) $\text{X} = \text{Cl}_2$, $\text{Y} = \text{CO}_2$

(C) $\text{X} = \text{Cl}_2$, $\text{Y} = \text{H}_2$

(D) $\text{X} = \text{H}_2$, $\text{Y} = \text{Cl}_2$

Sol.

21. $[\text{X}] + \text{H}_2\text{SO}_4 \rightarrow [\text{Y}]$ a colourless gas with irritating smell [JEE 2003]

$[\text{Y}] + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow$ green solution

$[\text{X}]$ and $[\text{Y}]$ are :

(A) SO_3^{2-} , SO_2

(B) Cl^- , HCl

(C) S^{2-} , H_2S

(D) CO_3^{2-} , CO_2

Sol.

22. A sodium salt of an unknown anion when treated with MgCl_2 with precipitate only on boiling. The anion is : [JEE 2004]

(A) SO_4^{2-} (B) HCO_3^- (C) CO_3^{2-} (D) NO_3^-

Sol.

23. A metal nitrate reacts with KI to give a black precipitate which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate is : [JEE 2005]

(A) Hg^{2+} (B) Bi^{3+} (C) Pb^{2+} (D) Cu^+

Sol.

24. A solution when diluted with H_2O and boiled, it gives a white precipitate. On addition of excess $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$, the volume of precipitate decreases leaving behind a white gelatinous precipitate. Identify the precipitate which dissolves in $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$. [JEE 2006]

(A) $\text{Zn}(\text{OH})_2$ (B) $\text{Al}(\text{OH})_3$
(C) $\text{Mg}(\text{OH})_2$ (D) $\text{Ca}(\text{OH})_2$

Sol.

25. CuSO_4 decolourises on addition of KCN, the product is : [JEE 2006]

(A) $[\text{Cu}(\text{CN})_4]^{2-}$
(B) Cu^{2+} get reduced to form $[\text{Cu}(\text{CN})_4]^{3-}$
(C) $\text{Cu}(\text{CN})_2$
(D) CuCN

Sol.

26. Consider a titration of potassium dichromate solution with acidified Mohr's salt solution using diphenylamine as indicator. The number of moles of Mohr's salt required per mole of dichromate is : (A) 3 (B) 4 (C) 5 (D) 6 [JEE 2007]

Sol.

27. The species present in solution when CO_2 is dissolved in water are - [JEE 2007]

(A) $\text{CO}_2, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-}$
(B) $\text{H}_2\text{CO}_3, \text{CO}_3^{2-}$
(C) $\text{CO}_3^{2-}, \text{HCO}_3^-$
(D) $\text{CO}_2, \text{H}_2\text{CO}_3$

Sol.

28. A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt(s) H is (are)-

(A) NH_4NO_3 (B) NH_4NO_2^- [JEE 2008]
(C) NH_4Cl (D) $(\text{NH}_4)_2\text{SO}_4$

Sol.

Paragraph for Question Nos. 29 to 31

When a metal rod **M** is dipped into an aqueous concentrated solution of compound **N**, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate **O**. Addition of aqueous NH_3 dissolves **O** and gives an intense blue solution. [JEE 2011]

29. The metal rod **M** is

(A) Fe (B) Cu
(C) Ni (D) Co

Sol.

30. The compound **N** is

(A) AgNO_3 (B) $\text{Zn}(\text{NO}_3)_2$
(C) $\text{Al}(\text{NO}_3)_3$ (D) $\text{Pb}(\text{NO}_3)_2$

Sol.

31. The final solution contains
 (A) $[\text{Pb}(\text{NH}_3)_4]^{2+}$ and $[\text{CoCl}_4]^{2-}$
 (B) $[\text{Al}(\text{NH}_3)_4]^{3+}$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (C) $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (D) $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Sol.

32. Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates
[JEE 2011]
 (A) CuS and HgS (B) MnS and CuS
 (C) MnS and NiS (D) NiS and HgS

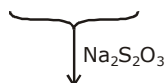
Sol.

33. For the given aqueous reaction, which of the statement(s) is (are) true ? **[JEE 2012]**

excess $\text{KI} + \text{K}_3[\text{Fe}(\text{CN})_6] \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{brownish-yellow solution}$



white precipitate + brownish-yellow filtrate



colourless solution

- (A) The first reaction is a redox reaction
 (B) White precipitate is $\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$
 (C) Addition of filtrate to starch solution gives blue colour.
 (D) White precipitate is solution in NaOH solution.

Sol.

34. Upon treatment with ammoniacal H_2S , the metal ion that precipitates as a sulfide is
 (A) $\text{Fe}(\text{III})$ (B) $\text{Al}(\text{III})$ (C) $\text{Mg}(\text{II})$ (D) $\text{Zn}(\text{II})$

Sol.

Paragraph for Question Nos. 35 to 36

An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl , gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in an ammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H_2O_2 in an aqueous NaOH medium.

35. The precipitate P contains

- (A) Pb^{2+} (B) Hg_2^{2+}
 (C) Ag^+ (D) Hg^{2+}

Sol.

36. The coloured solution S contains

- (A) $\text{Fe}_2(\text{SO}_4)_3$ (B) CuSO_4
 (C) ZnSO_4 (D) Na_2CrO_4

Sol.

ANSWER-KEY

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

Q.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	A	B	B	B	D	B	C	B	A	C	A	B	C	B	A
Q.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	D	C	D	C	B	B	A	C	C	B	B	D	B	B	B
Q.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
A	B	D	C	D	C	D	D	B	D	C	B	D	D	C	B
Q.	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
A	D	B	D	A	D	B	C	A	D	B	A	C	A	B	A
Q.	61	62	63	64	65	66	67	68	69	70					
A	A	D	B	B	D	A	C	A	B	C					

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

											1	2	3	4	5
											B	B	B	D	A
Q.	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A	D	C	B	B	B	D	A	A	C	B	B	C	C	A	C
Q.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
A	C	C	C	D	C	D	D	D	B	A	C	C	D	C	B
Q.		36	37							38					
A		D	(A) P,Q; (B) R; (C) P,Q,S; (D) P,Q,S							(A) S; (B) P,Q,R,S; (C) P,S; (D) P					

Answer Ex-III

SUBJECTIVE PROBLEMS (JEE ADVANCED)

Q.1 A,C

Q.2 B,C

Q.3 A,C

Q.4 A,B,C

Q.5 C,D

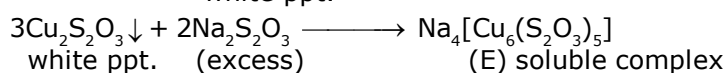
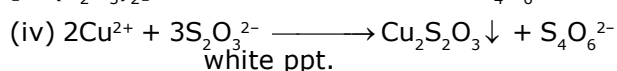
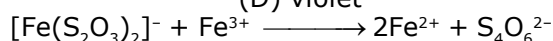
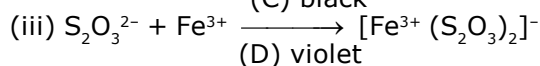
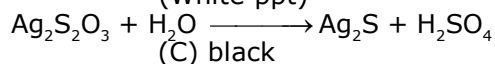
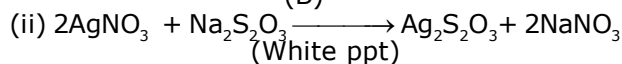
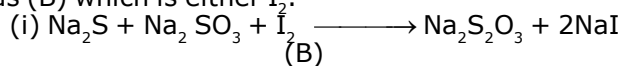
Q.6 A,C,D

Q.7 A,B,D

Q.8 B,C

Subjective

Q.1 The reactions indicate that the compound (A) is sodium thiosulphate. It is formed in step (i) by passing gas (B) which is either I_2 .



2. $A = \text{CoCl}_2$, $B = \text{CoS}$, $C = \text{K}_4[\text{Co}(\text{CN})_6]$, $D = \text{K}_3[\text{Co}(\text{CN})_6]$, $E = \text{Na}_3[\text{Co}(\text{CO}_3)_3]$
3. $A = 2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, $B = \text{CuO}$, $C = \text{CO}_2$, $D = \text{Cu}$, $E = \text{Cu}_2[\text{Fe}(\text{CN})_6]$, $F = \text{Ca}(\text{HCO}_3)_2$.
Azurite
4. The ore is chromite $\text{FeO} \cdot \text{Cr}_2\text{O}_3$.
- (i) $4\text{FeO} \cdot \text{Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \xrightarrow{\text{Lime}} 2\text{Fe}_2\text{O}_3 + 8\text{Na}_2\text{CrO}_4$
- (ii) $\text{Fe}_2\text{O}_3 + 6\text{HCl} \xrightarrow{\text{(B)}} 2\text{FeCl}_3 + 3\text{H}_2\text{O}$
 $4\text{FeCl}_3 + 4\text{K}_4\text{Fe}(\text{CN})_6 \xrightarrow{\text{(C)}} \text{Fe}[\text{Fe}(\text{CN})_6]_3 + 12\text{KCl}$
(D) Prussian blue
- (iii) $2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{(E)}} \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
- (iv) $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \xrightarrow{\text{(F) orange red}} \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$
- (v) $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{C}_2\text{O}_4 \xrightarrow{\text{(G) Blue crystal}} \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 6\text{CO}_2 + 7\text{H}_2\text{O}$
 $\text{Cr}_2(\text{SO}_4)_3 + 6\text{K}_2\text{C}_2\text{O}_4 \xrightarrow{\text{(G) Blue crystal}} 2\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3] + 3\text{K}_2\text{SO}_4$
5. $A = \text{CuSO}_4$, H_2O , $B = \text{CuSO}_4$, $C = \text{CuO}$, $D = \text{SO}_3$, $E = \text{Ag}$, $F = \text{NO}_2$

Answer Ex-IV

PREVIOUS YEARS PROBLEMS

LEVEL – I

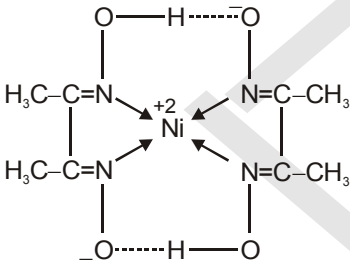
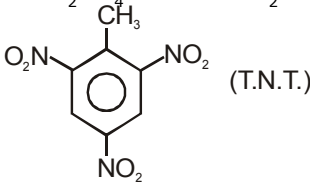
JEE MAIN

1. A 2. D 3. D

LEVEL – II

JEE ADVANCED

1. (i) $\text{FeSO}_4 + \text{BaCl}_2 \xrightarrow{\text{(A)}} \text{FeCl}_2 + \text{BaSO}_4$
white ppt. (B)
- (ii) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \xrightarrow{\Delta} \text{FeSO}_4 + \text{SO}_2 + \text{SO}_3$
(E) (C) (D)
brown residue
- (iii) $\text{Fe}_2\text{O}_3 + 6\text{HCl} \xrightarrow{\text{(E)}} 2\text{FeCl}_3 + 3\text{H}_2\text{O}$
(F) yellow solution
- (iv) $2\text{FeCl}_3 + \text{H}_2\text{S} \xrightarrow{\text{(H)}} 2\text{FeCl}_2 + 2\text{HCl} + \text{S} \downarrow$
(G)
- (v) $\text{FeCl}_3 + 3\text{NH}_4\text{SCN} \xrightarrow{\text{(H)}} \text{Fe}(\text{SCN})_3 + 3\text{NH}_4\text{Cl}$
2. $\text{Pb}_3\text{O}_4 + 4\text{HNO}_3 \rightarrow \text{PbO}_2 + \text{Pb}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$
(A) (B)
- $\text{Pb}(\text{NO}_3)_2 + 2\text{H}_2\text{O} \xrightarrow{2\text{KI}} \text{PbI}_2 + 2\text{KNO}_3$
(C)
- $\text{PbO}_2 \xrightarrow[+4\text{HNO}_3]{2\text{Mn}(\text{NO}_3)_2} \text{HMnO}_4 + 4\text{Pb}(\text{NO}_3)_3 + 2\text{H}_2\text{O}$
(B) (pink colour)
(D)
3. $A \rightarrow \text{NH}_3$ $B \rightarrow \text{CaCO}_3$
4. $\text{Bi}(\text{NO}_3)_3 + 3\text{K} \rightarrow \text{BiI}_3 \downarrow + 3\text{KNO}_3$
Black
- $\text{BiI}_3 + \text{KI} \rightarrow \text{K}[\text{BiI}_4]$
(excess) orange complex

5. $A = \text{NH}_4\text{NO}_3$; $B = \text{N}_2\text{O}$ & $C = \text{H}_2\text{O}$
 $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$
 $\text{P}_4 + 10\text{N}_2\text{O} \longrightarrow \text{P}_4\text{O}_{10} + 10\text{N}_2$
 (D)
6. (A) $\text{Hg}_2(\text{NO}_3)_2$ (B) Hg_2Cl_2
 (C) HgCl_2 (D) K_2HgI_4
 (E) Hg (F) $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$
7. Metal ion, Cu^{2+}
 $\text{Cu}^{2+}(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \longrightarrow \text{CuS} + 2\text{H}^+$
 (A)
 $2\text{Cu}^{2+} + 4\text{I}^-(\text{aq}) \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$
 (B)
8. $A = \text{MnSO}_4$, $B = \text{Na}_2\text{MnO}_4$,
 $C = \text{NaMnO}_4$, $D = \text{MnO}_2$,
 $E = \text{HMnO}_4$, $F = \text{BaSO}_4$
9. $A = \text{NaHSO}_3$, $B = \text{Na}_2\text{SO}_3$,
 $C = \text{Na}_2\text{S}_2\text{O}_3$, $D = \text{Na}_2\text{S}_4\text{O}_6$
10. $A = \text{HgI}_2$, $B = \text{KI}$, $C = \text{HgS}$, $D = \text{Hg}$
11. 
 hybridisation - dsp^2 ,
 M.M = 0, Diamagnetic
12. $A_1 = \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (malachite)
 $A_2 = \text{Cu}_2\text{S}$ (copper glance)
 $P = \text{CuI}_2$
 $G = \text{SO}_2 \uparrow$
13. $A = [\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$, $\text{MM} = \sqrt{35}$
 Pentaquaathiocyanato-S-iron (III) iron
 $B = [\text{FeF}_6]^{3-}$, $\text{MM} = \sqrt{35}$
 hexafluoroferrate (III) ion
14. $A = \text{conc. H}_2\text{SO}_4$, $B = \text{Br}_2$, $C = \text{NO}_2^+$
- D =  (T.N.T.)
 (Explosive)

15. $A - [\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
 $B - \text{HCl}$
 $\text{MCl}_4 - \text{TiCl}_4$
 Purple colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is due to d- transition.
16. C 17. B 18. B,C
19. D 20. C 21. A
22. B 23. B 24. A
25. D 26. D 27. A
28. A,B 29. B 30. A
31. C 32. A
33. ACD
 $\text{KI} + \text{K}_3[\text{Fe}(\text{CN})_6] \xrightarrow{\text{dil. H}_2\text{SO}_4} \text{I}_2 + \text{K}_4[\text{Fe}(\text{CN})_6]$
 (excess)
 $\text{I}_2 + \text{KI} \rightleftharpoons \text{KI}_3$ (brown -yellow sol)
 $\text{Zn}^{2+} + \text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 + \text{K}^+$
 (white ppt)
 or
 $\text{Zn}_2[\text{Fe}(\text{CN})_6] + \text{K}^+$
 (white ppt)
 $\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$
 $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 + \text{NaOH} \rightarrow \text{K}^+ + [\text{Zn}(\text{OH})_4]^{2-}$
 (white ppt) +
34. D
 Upon treatment with ammonical H_2S
 ZnS ppt as $\text{NH}_4\text{OH} + \text{H}_2\text{S}$ in group reagent for IVth group radicals.
35. A
 $\text{Pb}^{2+} + \text{Cr}^{3+} \xrightarrow{\text{dil. HCl}} \text{PbCl}_2 \downarrow + \text{CrCl}_3 \text{ (Q)}$
 white ppt.
 soluble in hot
 water insoluble in cold
36. D
 $\text{CrCl}_3 + \text{H}_2\text{S} + \text{dil HCl} \longrightarrow \text{No ppt.}$
 $\text{CrCl}_3 + \text{H}_2\text{S} + \text{NH}_4\text{OH} \longrightarrow \text{Cr}(\text{OH})_3(\text{s})$
 Green (R)
- $\left[\begin{array}{l} \text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-} \\ \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \\ 2\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} \end{array} \right]$
 S^{2-} ion conc. increases
 which causes ppt. ion
- $\text{Cr}(\text{OH})_3(\text{s}) + \xrightarrow[\text{oxidising agent}]{\text{NaOH} + \text{H}_2\text{O}_2} \text{Na}_2\text{CrO}_4$
 Yellow solution (R)